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Laser photodeposition of molybdenum oxide thin films from organometallic precursors

Kurt Andrew Olson

Iowa State University

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Iowa State University, 1989
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Laser photodeposition of molybdenum oxide thin films from organometallic precursors

by

Kurt Andrew Olson

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

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Ames, Iowa
1989
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1 INTRODUCTION

This dissertation represents the successful initiation of a research program in the area of laser deposition systems. Typical laser deposition systems are extremely complex exhibiting a wide variety of intertwined reaction and transport processes. In addition, elaborate apparatus and instrumentation are necessary to perform, control, and study laser depositions. A chemical engineering background offers a unique blend of skills and perspectives which is particularly well suited to the task of studying these systems. Although the ultimate goal of this research was to study and understand some particular chemical system, the initial goals were to conceive, design, and develop both apparatus and experimental techniques for studying laser deposition systems in general.

1.1 Initial Goal: Laser Deposition Systems

Laser deposition systems are comprised of complex combinations of fluid flow, gas phase photochemistry, mass transport, surface chemistry, surface reaction, unsteady
state heat transfer, and surface diffusion processes. Typically, studies of laser deposition of thin films have tended to be demonstrative in nature and analyses are often limited to evaluations of film performance and atomic compositions. There exists an obvious need for increased understanding of the chemical and physical relationships between the resulting film, reactant and by-product properties, and deposition conditions. The initial goal of this research was to develop techniques to allow the elucidation of characteristic processes which occur in laser deposition systems. The emphasis of these studies was on identifying the chemical and physical form of the species which result from various deposition conditions in order to dissect and understand the overall process.

1.2 Specific Goal: Thin Film Materials

Laser deposition of refractory metals from metal hexacarbonyls is complicated by the incorporation of carbon and oxygen contamination derived from the CO ligand by-product. This contamination seems to be predictable based on the known tendency of refractory metals to dissociate CO. One solution to the problem is to utilize a precursor which upon decomposition produces fragments which interact in a less detrimental manner with the metal film. Another approach is to use the hexacarbonyl to produce a different
film which is more inert with respect to the by-product CO. Refractory metal oxides for example, over a wide range of temperatures, do not dissociate carbon oxides.

Amorphous molybdenum and tungsten trioxides exhibit many properties which are useful in thin film applications. Crystalline MO$_3$ (M = Mo or W) films have also been produced. Many crystalline phases of "reduced" ($2 \leq x < 3$) MO$_x$ compounds exist, but with the exception of MoO$_2$, thin films of the "reduced" oxides have never been reported. This is surprising because these materials exhibit interesting optical properties. In addition, due to their layered structures, these compounds exhibit anisotropic electrical properties and behave as low dimensional conductors (1-D, or 2-D) which could prove extremely useful in microelectronics applications.

During the course of the research reported in this dissertation, experiments attempting to deposit refractory metal oxide films by laser photodeposition led to the discovery that under certain conditions crystalline "reduced" molybdenum oxide films could be formed. As a result of this, the specific goal of this research was to elucidate the mechanisms by which these films were produced.
This chapter contains a review of the literature pertinent to the research presented in this dissertation. The first section describes the laser deposition process. In the second section, literature dealing with refractory metal carbonyl systems is reviewed. The third section presents a discussion of the molybdenum oxides and alternative organomolybdenum precursors studied in this work. The last section briefly discusses the recent advances in the Raman spectroscopic technique which account for its utility in this work.

2.1 Laser Deposition: General Description

2.1.1 Introduction to Laser Deposition

The initial investigations of laser induced chemical processing of surfaces and thin films were reported in 1978 [1] and 1980 [2]. Since then interest in the field has grown at a very rapid rate. A wide variety of chemical systems and laser induced effects have been investigated.
Many reviews and conference proceedings dealing with laser induced processes have been published (see for example References [3-10]). The recent "Springer Series" books on laser processes [11-13] are excellent references which present comprehensive discussions of virtually all of the processes which are currently known to occur during laser processing at interfaces. Due to the existence of the above mentioned publications, the discussion of laser photodeposition which follows will be limited to an outline of the major concepts including a few noteworthy examples.

Laser deposition is a process in which laser light causes the deposition of a material by initiating reactions in a layer of chemical reactants on or near a surface. This process is depicted in Figure 2.1. The function of the laser is to initiate a reaction by photolytically and/or thermally inducing the dissociation of a precursor molecule. Most commonly the desired deposit is a metallic film and the precursor is an organometallic compound. Compounds such as metal oxides, nitrides, and silicides can be deposited by including secondary reactants such as oxygen, ammonia, and silane.

Laser deposition has many process characteristics which are desirable in the production of microelectronic devices. The advantage of a "one-step" patterned deposition process by "direct writing" or image projection over conventional multistep lithographic methods is one of the most attractive
Figure 2.1 Schematic of laser deposition processes
features of laser deposition. In addition, laser depositions can be performed at significantly lower substrate temperatures than many conventional techniques such as chemical vapor deposition. Low temperature processes preserve the integrity of the microelectronic device structures and materials produced by previous processing steps. Photolytic processes, in particular, have the additional capability of separating the control of the chemical reactions from the ultimate morphology of the deposited film (which is determined by the surface temperature). Some of the disadvantages of laser processing are increased complexity of operation, and complicated reactor design necessary to prevent fouling of the deposition cell window(s).

2.1.2 Reactant Molecules Source Phase

One of the main characteristics of any laser deposition system is the phase in which the initial reactions take place. In some systems gas phase precursor molecules are "activated" and are transported to the surface. In systems with secondary reactants it is possible for additional gas phase reactions to occur before the "activated" precursors deposit on the surface of the substrate or previously deposited film. These intermediates are subsequently deposited.
Precursor molecules which are adsorbed to the substrate or deposit surface are another possible source for deposition processes. In these systems molecules are "activated" in the region where the laser light impinges on the surface. As the molecules decompose or react to give the desired material, the supply is replenished by molecules which adsorb from the gas phase and/or diffuse over the surface. A simple (in concept at least) experiment which can unequivocally determine whether a particular system is gas phase or adsorbed phase dominant is parallel beam deposition. Gas phase activation processes can be completely isolated by passing the laser beam parallel to the surface thereby eliminating any laser induced activation of adsorbed molecules. This technique, however, is inadequate for systems which depend on laser surface heating for activation of the precursor molecules.

The studies of cadmium deposition from dimethylcadmium (DMCd) and aluminum from trimethyl aluminum (TMA) performed by Ehrlich and Osgood [14,15] provide examples of systems which can exhibit the different types of source behavior. In this work the behavior of the deposition rate was studied as a function of substrate temperature. It is expected that small changes in surface temperature could have a large effect on the number of adsorbed molecules but would have no significant effect on the concentration of gas phase molecules. The deposition rate of Cd was relatively
Insensitive to substrate temperature while the aluminum system showed a strong dependence on substrate temperature. These results indicate that adsorbed TMA molecules were the source of aluminum atoms which were deposited while the DMCd system was gas phase dominant.

The dependence of deposit growth rate on the laser spot size (diameter) has also been used to determine which phase, gas or adsorbed, is the dominant source. Gas phase molecules can diffuse to a spot on the surface in three dimensions while adsorbed molecules are limited to two-dimensional diffusion. This difference in dimensionality of the two systems ultimately results in different dependences of the rate on the system's characteristic length (spot diameter) (see for example Wood et al. [16]).

Solid organometallic films are a recent addition to the list of possible sources for laser depositions. Solutions of a dissolved organometallic have been applied (spun-on) to surfaces and allowed to cure in much the same manner as conventional photoresists. The resulting solid film is decomposed with a focused laser leaving the metal behind. Palladium and platinum have been deposited by this technique (see Gross et al. and Gupta et al. in [3]).
2.1.3 Activation Processes

The mechanism by which the precursor molecule is "activated" is another important characteristic of laser deposition systems. Although the overall description of many laser deposition systems involves combinations of photolytic and thermal processes, the initial activation process can usually be attributed to either a purely photolytic or a purely thermal process.

2.1.3.1 Photolytic activation In photolytically activated systems, the photochemical properties of the precursor are obviously important. The most important property is the absorption cross section, $\sigma$, at the laser wavelength, $\lambda$. This quantity, in combination with the photon flux supplied by the laser, determines both the number of precursor molecules which are activated and ultimately the amount of material that is deposited. Photolytic activation can occur either in the gas phase or in adsorbed layers. It is possible for $\sigma$ to change on adsorption as illustrated by Rytz-Froideveaux et al. [17] for the dimethylcadmium laser deposition system.

Another important characteristic of a particular precursor is the path which photodissociation follows. The identity and number of specific bonds broken determine not only the secondary reactions but also the ultimate composition of the deposit. Due to the popularity of the
study of metal deposition systems, studies of secondary reactions are relatively rare. An excellent example of the importance of secondary reactions is reported by Gupta, West, and Beeson [18,19]. In this work mass spectrometry was used to monitor the products of secondary reactions during the laser induced deposition of TiSi$_2$ from TiCl$_4$ and SiH$_4$.

2.1.3.2 Thermal activation In thermally activated systems, thermal decomposition behavior is the most important characteristic of the precursor. In these systems laser radiation induces thermal reactions by one or both of two mechanisms. The most common mechanism is the laser induced heating of the substrate. Excitation of molecular vibrations with infrared laser radiation can also lead to thermal decomposition. Thermal reactions tend to give reaction products which are thermodynamically favored whereas photolytic processes can lead to non-thermodynamically favored product distributions. The references of Gupta, West, and Beeson [18,19] provide interesting studies of thermal reactions induced by molecular absorption of infrared (CO$_2$, 10.6 $\mu$m) laser radiation as compared to photolytic reactions induced by UV (ArF Excimer, 193 nm) radiation.

2.1.3.3 Laser induced surface heating Laser light, because of its high intensity, can lead to significant temperature changes in a solid material. The
magnitude of the temperature rise at the surface of a material is governed by several factors. Optical (absorption coefficient, $\alpha$ and reflectivity, $R$) and thermal (thermal conductivity, $k$ and heat capacity, $C_p$) properties of the surface combine with the intensity and duty cycle of the laser beam to determine the resulting surface temperature. Models for continuous wave and pulsed laser heating are presented in [12]. The particular model which applies to the pulsed UV laser and silicon substrate used in this work will be discussed in Chapter 5 and Appendix B.

2.1.3.4 Hybrid: photolytic supply and thermal "curing" In actuality, most photolytically activated systems have a thermal component as well. Laser surface heating, in many cases, is necessary to stimulate the desorption of undesirable organic fragments or to induce the densification of the previously deposited material. An excellent example of this has been reported by Gilgen et al. [20]. In this work it was shown that deposition of tungsten, molybdenum, and platinum from $\text{W(CO)}_6$, $\text{Mo(CO)}_6$, and a fluorinated acetylacetonate platinum compound respectively, were activated photolytically. However, high quality metal deposits could only be obtained when a thermal ("pyrolytic") process was involved as well.
2.2 Laser Deposition of Refractory Metals from Carbonyls

Refractory metals (Mo, W, and Cr) have a wide variety of uses as thin films in the fabrication of microelectronic devices (see for example [21-23]). Until the work presented in this dissertation, refractory metals had been laser deposited with the sole intention of producing metallic films. Metal carbonyls in particular have received extensive attention due to their known photochemical activity and relative ease of handling. The sections which follow focus specifically on Mo(CO)\textsubscript{6} systems but also refer to related systems when information on Mo(CO)\textsubscript{6} is unavailable.

2.2.1 Properties of Refractory Metal Hexacarbonyls

2.2.1.1 Thermochemistry Thermal decomposition of Mo(CO)\textsubscript{6} begins at approximately 130-150 °C [24]. Skinner and Connor [25] have reported that for transition metal organometallics the metal-carbon bond is weakest in metal carbonyls. The mean and first bond dissociation energies for Mo(CO)\textsubscript{6} have been reported as 36 and 40 kcal/mol, respectively [26,27]. The heat of formation of gaseous Mo(CO)\textsubscript{6} is -219 kcal/mol [28].

2.2.1.2 Photochemistry Two UV absorption studies have been used to measure the absorption cross section, $\sigma$,
of Mo(CO)$_6$ at 193 nm. Iverson and Russel [29] report a value of $1.8 \times 10^{-18}$ cm$^2$ while Flynn et al. [30] report $1 \times 10^{-18}$ cm$^2$ (after converting their nonstandard definition of $\sigma$). The dissociation of refractory metal hexacarbonyls in low temperature matrices has been studied by infrared and UV-visible absorption spectroscopy [31,32]. In these studies a medium pressure Hg lamp was used to dissociate M(CO)$_6$ ($M =$ Mo, W, Cr) and the formation of sub-carbonyl species was monitored with time. The primary product was determined to be M(CO)$_5$ while secondary products (due to additional absorption), such as M(CO)$_4$ and M(CO)$_3$, were also observed.

Investigations of gas phase photodissociation would be more relevant to laser photodeposition processes. Such investigations have been performed by Fletcher and Rosenfeld [33-35] and by Tyndall and Jackson [36,37]. Both groups have focused on the gas phase photodissociation of Cr(CO)$_6$ at 248 nm. The energy provided by one 248 nm photon is 115 kcal/mol (5 eV) which is more than enough to account for the breaking of 2 metal ligand bonds ($D_{\text{mean}} = 25.6$ kcal/mol, $D_1 = 37$ kcal/mole).

Fletcher and Rosenfeld have investigated the formation of the primary photoprodut resulting from absorption of one 248 nm photon. Time resolved infrared laser absorption was used to determine rate constants for the various secondary reactions that occurred. The primary photoprodut was found
to be "vibrationally hot" \(\text{Cr(CO)}_4\). Rate constants for the subsequent reactions shown in Equation 2.1 are presented in

\[
\text{Cr(CO)}_4 + L \rightarrow \text{Cr(CO)}_4L \quad \text{(Eq. 2.1)}
\]

Table 2.1. These rate constants span the range of approximately 0.1 to 1.0 times the hard sphere collision rate clearly indicating that the \(\text{Cr(CO)}_4\) species is extremely reactive. Based on the proposed dependence on ionization potential, the rate constant for \(\text{O}_2\) (ionization potential 13.58 eV [38]) would be expected to be similar to \(\text{CO}\) and \(\text{C}_2\text{H}_4\) corresponding to approximately one half of the hard sphere collision rate. The authors also indicate that visible emission observed on irradiation of \(\text{Cr(CO)}_6\) with 193 nm radiation is the result of a multiphoton process. No information on the primary photoprodust at 193 nm was presented.

Tyndall and Jackson focus mainly on the multiphoton dissociation (MPD) mechanisms which lead to the production of metal atoms. The energetic states of the atoms produced were studied by detecting the emission from the excited atoms. Reference [36] includes brief discussions of \(\text{Cr(CO)}_6\) at 193 and 351 nm as well as \(\text{Mo(CO)}_6\) at 193 and 248 nm. However, the experiments described were not designed (and hence unable) to determine the primary photoprodust or rate constants of secondary reactions.
Table 2.1 Reaction rate constants for the reaction of various ligands with Cr(CO)$_4$ including proposed correlation with ionization potential (from Fletcher and Rosenfeld [35])

<table>
<thead>
<tr>
<th>L</th>
<th>Rate Constant $k$ (torr$^{-1}$ s$^{-1}$)</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_2$)$_2$NH</td>
<td>$1.5 \pm 0.2 \times 10^7$</td>
<td>8.24</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$1.1 \pm 0.2 \times 10^7$</td>
<td>10.20</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>$9.1 \pm 1.4 \times 10^6$</td>
<td>10.50</td>
</tr>
<tr>
<td>CO</td>
<td>$7.5 \pm 1.5 \times 10^6$</td>
<td>14.00</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$1.6 \pm 0.4 \times 10^6$</td>
<td>15.42</td>
</tr>
<tr>
<td>D$_2$</td>
<td>$1.6 \pm 0.4 \times 10^6$</td>
<td>15.47</td>
</tr>
<tr>
<td>Ar</td>
<td>no reaction</td>
<td>15.8</td>
</tr>
<tr>
<td>He</td>
<td>no reaction</td>
<td>24.48</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>$1.8 \pm 0.3 \times 10^7$</td>
<td>-----</td>
</tr>
<tr>
<td>O$_2$</td>
<td>not studied</td>
<td>13.58</td>
</tr>
</tbody>
</table>

(a) Reference [34]  
(b) Reference [38]
2.2.2 Laser Deposition of Refractory Metal Films

2.2.2.1 Mechanisms  Laser photodeposition has been used to deposit refractory metal films from their respective hexacarbonyls [20, 39-41]. In all reported cases a thermal component was necessary to produce films with acceptable levels of carbon and oxygen contamination. In the absence of laser heating [20] or elevated surface temperatures [40], the resulting films are highly contaminated. The process is known to be photolytically activated in the gas phase for wavelengths from 257 nm to 193 nm. The major problem with this process is the difficulty in obtaining films which are not contaminated with carbon and oxygen.

2.2.2.2 Contamination by C and O  The difficulty in obtaining carbon and oxygen free metal films is not surprising when the interactions of CO and molybdenum are considered. Upon adsorption onto single crystal molybdenum surfaces, CO is known to dissociate into atomic C and O. This occurs over a wide range of temperatures and certain states of CO remain bound up to 900-1000 °C (see for example [42-46]).

The photodecomposition of adsorbed Mo(CO)$_6$ has been investigated with the intent of understanding the mechanism by which carbon and oxygen contamination arises in photodeposited molybdenum films. Creighton [47,48] has used
temperature programmed desorption to show that Mo(CO)$_6$
physisors on Si(100) and desorbs in vacuo above 210-230 °K. The decomposition of the adsorbed material (150 °K)
upon exposure to 248 nm or 193 nm radiation was shown to be
purely photolytic. Auger electron spectroscopic analysis of
the deposit showed considerable carbon contamination which
the author attributed to the dissociation of one CO ligand
per Mo(CO)$_6$ decomposed.

Gluck and co-workers have used high resolution electron
energy loss spectroscopy (HREELS) and elaborate laser
induced desorption experiments to study the decomposition of
Mo(CO)$_6$ on Si(111)[49-51]. They also report that 257 nm
photons led to purely photolytic decomposition of adsorbed
Mo(CO)$_6$. In addition, HREELS showed the growth of adsorbed
CO on exposure of the adsorbed Mo(CO)$_6$ to photons.

2.3 Molybdenum Compounds

2.3.1 Molybdenum oxides

2.3.1.1 Uses Molybdenum and tungsten oxides,
(MO$_x$ where $x \leq 3$, $M = Mo$ or W) have been used in a variety
of thin film applications. Amorphous MO$_3$ films have
received much interest due to their photo-, chemi-, and
electrochromic [52] and photoelectric [53] properties.
These materials can function as flat panel video displays
Molybdenum oxides are also known to be highly active catalysts. Aspects of their catalytic behavior which are relevant to the research presented in this dissertation will be discussed elsewhere in this chapter.

2.3.1.2 Structures and properties  A wide range of crystal structures is known for $\text{MoO}_x$ where $2 \leq x \leq 3$. Crystalline phases with $0 < x < 2$ have not been observed to date. The basic unit common to most $\text{MoO}_x$ phases is the octahedron formed by six oxygens coordinated to one molybdenum. Different structures and oxidation states can be formed by changes in the manner in which the octahedra are connected. Corner-sharing and edge-sharing are the common descriptions of the $\text{MoO}_6$ octahedra. Another common type of coordination for $\text{MoO}_x$ is tetrahedral where four oxygens are coordinated to one molybdenum.

$\text{MoO}_2$ is generally described as having a distorted rutile type structure [62]. Figure 2.2 shows the idealized structure of $\text{MoO}_2$ consisting of strings of edge-sharing octahedra which are connected to adjacent strings by corner-sharing. Each of the oxygens is shared by three molybdenum atoms. Crystalline $\text{MoO}_2$ is dark brown while dark gray when
Figure 2.2  Idealized structure of MoO$_2$.
MoO₂ exhibits metallic electrical properties with a bulk resistivity of 88–200 μΩcm [63].

α-MoO₃ is the most commonly occurring form of MoO₃. Its structure, shown in Figure 2.3a, is generally described as a layer structure with each layer comprised of two "sheets" of octahedra [64]. The two "sheets" are "collapsed" so that octahedra of the upper "sheet" share two edges with the octahedra in the lower sheet. In this description there are three different types of oxygens including one singly coordinated, two doubly coordinated, and three triply coordinated. This description can be expressed by \( \text{MoO}_{1/1}^{1/2} \text{O}_{2/2}^{2/3} \) [65]. Alternatively the structure can be described in terms of pairs of strings of corner-sharing tetrahedra [64]. Crystalline α-MoO₃ is optically transparent (or yellowish for large crystals) and white as a powder. It is electrically insulating.

β-MoO₃ is a recently discovered [65–67] ReO₃-related structure. The idealized structure is shown in Figure 2.3b. This structure is comprised of sheets of corner-sharing octahedra. Coordination between sheets is also corner-sharing. This type of structure is sometimes expressed as \( \text{MoO}_{6/2} \) indicating that each of the six oxygens per octahedron is coordinated to two Mo atoms. This structure is metastable and known to "collapse" [66] to α-MoO₃ over the range of 250 – 400 °C. β-MoO₃ is bright yellow and,
Figure 2.3  Idealized structures of $\alpha$-MoO$_3$ (a), and $\beta$-MoO$_3$ (b)
based on its similarity to WO$_3$, would be expected to behave as an electrical insulator.

$\gamma$-Mo$_4$O$_{11}$ and $\eta$-Mo$_4$O$_{11}$ have structures which are comprised of "slabs" of corner-shared octahedra similar to $\beta$-MoO$_3$ alternating with "sheets" of tetrahedra. These structures, first reported by Magneli [68,69] and studied in detail by Kihlborg [70,71] and Ghedira et al. [72], are the first in a series of compounds with the general formula Mo$_n$O$_{3n-1}$. Many other MoO$_x$ crystalline phases with 2 < x < 3 exist but will not be discussed here (see for example [73 - 79]). The "slabs" of Mo$_4$O$_{11}$ are three octahedra thick as shown in Figure 2.4. In the orthorhombic $\gamma$ phase (Figure 2.4a), the orientation of the "slabs" alternates while in the monoclinic $\eta$ phase (Figure 2.4b), all of the "slabs" are aligned in the same direction. An additional difference in structure is the shape and size of the "tunnels" formed by the tetrahedra in the connecting layer. The "tunnels" are pentagonal in the $\gamma$ phase and hexagonal in the $\eta$ phase.

Both phases of Mo$_4$O$_{11}$ exhibit anisotropic optical properties with the bc plane exhibiting a reddish-purple color while the other two faces are gold colored. Shimoda and co-workers have reported polarized reflectance spectra of $\gamma$-Mo$_4$O$_{11}$ which show that the dependence of reflectivity (bc plane) on wavelength for light polarized parallel to the b axis is markedly different from that polarized parallel to
Figure 2.4 Idealized structure of \( \gamma-Mo_4O_{11} \) (a), and \( \eta-Mo_4O_{11} \) (b) showing slabs of octahedra connected by sheets of tetrahedra.
the c axis. This results in the surface appearing different colors for the two polarizations [80,81].

Perhaps even more interesting is the observed anisotropic electrical behavior of γ-Mo₄O₁₁. Recently there has been a growing interest in "low-dimensional" conductors and electronic transitions in layered materials [82]. γ-Mo₄O₁₁ is a "two-dimensional" conductor with resistivities of approximately 5 x 10⁻⁴ and 8 x 10⁻⁴ in the b and c directions while the resistivity in the a direction, 5 x 10⁻² Ωcm, is two orders of magnitude larger [83,84].

Mo₈O₂₃ is also comprised of slabs of MoO₆ octahedra but, instead of MoO₄ tetrahedra, the connecting layer consists of edge shared octahedra as shown in Figure 2.5 [75]. Mo₈O₂₃ also exhibits anisotropic conduction properties with room temperature resistivities of 1.5 x 10⁻², 1 x 10⁻¹, and 1.8 Ωcm for the a, c, and b directions respectively [83].

2.3.1.3 Formation temperatures and thermodynamics

Figure 2.6 shows formation temperatures (from [71]) for some molybdenum oxide compounds. As shown, η-Mo₄O₁₁ is thermodynamically unstable with respect to the γ phase and transforms above approximately 630 °C. γ-Mo₄O₁₁ is stable to temperatures as high as 800 °C. The difference in the heats of formation of Mo₄O₁₁ [85] versus (3 MoO₃ + MoO₂) [86] as depicted in Equation 2.2 is very small and probably does

\[ \text{Mo}_4\text{O}_{11} \rightarrow 3 \text{MoO}_3 + \text{MoO}_2 \quad \Delta H_{298} = -4 \text{ kcal/mol} \quad (\text{Eq. 2.2}) \]
Figure 2.5  Idealized structure of Mo$_8$O$_{23}$ showing edge-shared octahedra connecting layer
Figure 2.6 Formation temperatures for molybdenum oxides of various compositions (from Kihlborg [71])
not provide a significant driving force in this system at low temperatures.

2.3.1.4 Syntheses and crystal growth  
Previous to the work reported in this dissertation, bulk solid crystalline MoO$_4$ compounds had been synthesized by three methods. The simplest and most common method of producing crystalline MoO$_4$ is by solid state synthesis [71]. This technique involves heating intimate mixtures of stoichiometric amounts of MoO$_3$ and MoO$_2$ (or MoO$_3$ and Mo metal) to temperatures from 550-610 °C (η phase) and 630-750 °C (γ phase) for periods of a few days (shorter for the higher temperatures). Large crystals have been grown by the temperature gradient flux technique [80] and chemical vapor transport from previously synthesized crystalline MoO$_4$ [87]. In all cases the temperatures were similar to the solid state technique. Svensson and Kihlborg [67] have reported the formation of β-MoO$_3$ by the slow oxidation of γ-MoO$_4$ at temperatures from 180-270 °C.

2.3.1.5 Thin film deposition  
With very few exceptions, the deposition of thin films of molybdenum oxides has been restricted to amorphous MoO$_3$ films. Amorphous MoO$_3$ films have been produced by thermal evaporation of MoO$_3$ [59,88], reactive r.f. sputtering of MoO$_3$ [66,89] and Mo [61] targets in oxygen atmospheres, and by oxygen plasma enhanced chemical vapor deposition from Mo(CO)$_6$ [90]. Saito et al. [88] have observed
"microcrystalline" domains in amorphous (characterized by X-ray diffraction) MoO$_3$ films. On annealing, the films exhibit increased crystallinity (sharper diffraction patterns), but the "microcrystalline" domains appear to remain the same size. The authors attribute this to a "relaxation" of the distorted structure of the "as-deposited" film as opposed to growth of crystallites.

Crystalline $\alpha$ and $\beta$-MoO$_3$ thin films have been deposited by r.f. sputtering in argon-oxygen atmospheres [66]. In this work the resulting crystallinity of the deposited film was attributed to the mobility of surface species during deposition. On low mobility ($T < 100$ °C) surfaces, only amorphous material was deposited. The authors maintain that the phase with higher thermodynamic stability ($\alpha$-MoO$_3$) can be produced at lower than normal temperatures by "artificially" inducing surface mobility with additional impinging Ar$^+$ ions. However, the experiments leading to this interpretation were performed under conditions where the surface temperature was poorly characterized. So and co-workers [61] have reported the production of MoO$_x$ where $x < 2$ and report that the films contain crystalline Mo and MoO$_2$ after annealing at 600–800 °C. The authors report that the as-deposited material contains bcc Mo which indicates that the effective surface mobility in the system corresponds to an effective temperature of at least 400 °C.
2.3.1.6 Reactivity/catalysis of oxidized molybdenum  Obviously in photodeposition systems the interaction between the deposited film and the reaction by-products must be considered. For the deposition of molybdenum oxide films from Mo(CO)$_6$, the interactions of CO with oxidized molybdenum will be important in determining the likelihood of producing contaminant-free films. The inhibition of CO adsorption on single crystal molybdenum surfaces has been reported by Ko and Madix [91] and Deffeyes et al. [92]. Other interactions of CO on MoO$_x$ relating specifically to processes which occur during photodeposition will be presented in context in the discussion section of Chapter 5.

2.3.2 Alternative precursors

2.3.2.1 Desirable properties  Molybdenum hexacarbonyl is not the only possible precursor for molybdenum or molybdenum oxide films. To be useful in laser photodeposition systems, precursors must possess a number of properties. A precursor must be thermally stable in the deposition apparatus and exhibit a vapor pressure high enough so that sufficient amounts can be transported to the reactor. A more subtle requirement is that the reaction by-products (fragments) do not interfere (or can be prevented
from interfering) with the formation of the desired product film.

2.3.2.2 Molybdenum allyl  The lack of oxygen in molybdenum allyl, Mo(C$_3$H$_5$)$_4$, makes it a feasible candidate for a metallic film precursor. It seems possible that, by depositing in a hydrogen atmosphere, the organic fragments could be completely removed from the deposited material. This compound has been studied extensively for the production of supported catalysts [93,94]. The compound is expected to have reasonable volatility and thermal stability as it can be purified by sublimation in a high vacuum at 60 - 70 °C [95]. It has also been shown to be photolytically active, undergoing loss of ligands on exposure to UV radiation [96].

2.3.2.3 Molybdenum trifluoroacetate dimer  While probably not useful for the production of metallic films, refractory metal compounds in which the ligands are bound to the metal through oxygen could be considered as precursors for metal oxide films. Dimolybdenum tetraacetate, Mo$_2$(O$_2$CCH$_3$)$_4$, is one such compound. This compound is also interesting due to the multiple bond between the two Mo atoms. However, its vapor pressure is much too low [97] to be useful as a gas phase source and its solubility is too low to be used as a "spun-on" solid film.

By fluorinating the acetate ligand, the vapor pressure [97], solubility, and stability of the compound increase
drastically. The fluorinated acetate, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, has been reported by Cotton and Norman [98]. In addition, a recent study [99] has reported preliminary results on the gas phase photofragmentation of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The authors report that $\text{Mo}_2\text{O}^{+}_{1-4}$ species are formed by multiphoton ionization at 337 nm while species created by longer wavelengths are more likely to exhibit rupturing of the metal-metal bond.

Tetraformates and other tetracarboxylates of molybdenum [100], as well as similar compounds of other metals, such as Cr-Cr, or mixed metals Cr-Mo [101], have been reported. The added dimension of the metal-metal bond of this class of materials makes them very interesting as candidates for the production of reduced refractory metal oxides.

2.3.2.4 Fluorinated molybdenum acetylacetonate

Recently, fluorinated acetylacetonate copper compounds have been used as volatile precursors for the deposition of metallic copper films (see for example [102]). Acetylacetonate compounds of molybdenum, such as $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ and $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$, are known [103]. These compounds have very low vapor pressures and solubilities. A fluorinated acetylacetonate molybdenum compound has been reported recently [104] and should possess enhanced volatility and solubility. Fluorinated acetylacetonate compounds are formed by an extremely large group of metals including Rh, Cr, Fe, Al, Th, Ni, Co, Nd, Zn, Mn, Sr, and Cu [105] and
thus represent an exciting prospect for depositing a wide variety of materials.

2.4 Raman Spectroscopy

2.4.1 Raman spectroscopy: general

The Raman effect occurs when a photon scatters after collision with a molecule. The incident photon can lose (Stokes process) or gain (Anti-Stokes) energy from the molecule during the scattering process and thus change in frequency. This inelastic scattering is much less likely to occur than the elastic scattering and consequently the Raman effect usually results in weak signals which are difficult to detect. The change in the frequency of the photon is equal to the vibrational frequency of the particular chemical bond ("electron cloud") with which the photon interacted. The Raman effect can also be due to the interaction of photons with lattice vibrations in a crystal. In addition, due to the polarization of the incident laser beam which excites the molecules or crystal, information related to the molecular symmetry and/or crystal orientation can be obtained.

With the recent advances in optical multichannel photodetection [106-108], Raman spectroscopy has become a powerful technique, sensitive enough for the study of thin
films and of gases adsorbed on planar surfaces. Previous to these developments "surface" Raman spectroscopy had been limited to the study of gases adsorbed on high surface area materials [109] and of surface enhanced Raman effects which exhibit anomalously large signals in a limited number of systems (see for example [110]). An example of Raman spectroscopy of thin films on semiconducting substrates is given by Tsang et al. [111].

2.4.2 Raman spectroscopy of adsorbed monolayers

Greenler was the first to present the theory of the electromagnetic interactions between photons and surfaces as they related to vibrational spectroscopies [112]. The reflection of light from a planar metallic surface leads, through constructive interference, to an increase in the electric field at the surface. This enhanced electric field in turn can lead to enhancement of the Raman effect for molecules on or near the surface. The theory has been supported by experiments reported by Mullins and Campion [113]. Several examples of Raman studies of molecules adsorbed on planar surfaces have been reported. A few example systems are CO and Ni(100) [114], nitrobenzene on AlO_x [115], and pyridine on Ni(111) [116].
3 EXPERIMENTAL PROCEDURES AND APPARATUS

This chapter contains the details of the experimental apparatus and procedures used in performing this research. The first section describes the actual laser deposition experiments. The second presents the techniques used to prepare the molybdenum oxide standards and prospective alternate source molecules. The third section describes the advanced Raman spectroscopic techniques while the fourth outlines various other characterization methods.

3.1 Laser Photodeposition

3.1.1 Apparatus

An overall schematic of the laser deposition system designed and built for this work is shown in Figure 3.1. The system is comprised of three main parts including a feed system for supplying inert and reactant gases, a laser deposition cell, and an excimer laser and optics system. Also included is a mass spectrometer for monitoring reactant concentrations.
Figure 3.1 Laser deposition system overall schematic
3.1.1.1 Gas feed system Reactant and window flushing gas streams were generated and controlled by the gas feed system shown in Figure 3.2. In addition to the three inert gas lines (Helium, zero grade Air Products) necessary for window flush, reactant carrier, and reactant dilution streams, two controlled streams were available for gases such as oxygen (Air Products), hydrogen, and carbon monoxide. Source gases were passed over oxygen-removal columns (BASF copper oxide catalyst)(excepting the oxygen source), moisture traps (molecular sieve 4 Å, Aldrich), and particle filters (Nupro 7μ). The system was constructed with 1/4" and 1/8" stainless steel tubing, valves (Whitey and Nupro) and compression fittings (Swagelok) with the exception of the copper tubing used for the oxygen-removal traps, moisture traps and window flush preheat coil. Mass flow controllers (Tylan model FC280 and model RO-28 readout box) were used to control flowrates.

3.1.1.2 Saturator and scavenger Gaseous organometallic molecules were generated by passing helium over solid molybdenum hexacarbonyl (Alfa, 99% purity, remainder mostly Mo metal) using the saturator arrangement shown in Figure 3.3. All gas lines and cell surfaces downstream of the saturator oven were maintained at an elevated temperature with resistance heating tapes to prevent the organometallic precursor from recrystallizing in the lines. Temperatures were monitored with chromel-alumel
Figure 3.2 Gas feed system
Figure 3.3 Saturator oven for organometallic precursors
thermocouples and a digital readout (Omega Engineering model 199A). Effluent gas from the deposition cell was fed to a heated scavenger reactor (silicon carbide inside 1/2" copper pipe) in order to thermally decompose any remaining organometallic molecules before venting to a fume hood.

3.1.1.3 Deposition Cell The stainless steel laser deposition cell shown in Figure 3.4 was designed to meet a wide variety of criteria. Of primary concern was the need to isolate the reactant gas to minimize deposition on (destruction of) the cell windows. The inner channel directs reactant gas over the substrate while the outer "window flush" acts as a barrier between the reactant molecules and the window surfaces. Three windows allow the laser beam to impinge directly on the substrate or pass parallel over the substrate. Low vapor pressure cement (Torr Seal®) was employed to mount and seal the quartz (Esco Products Si-UV-B grade) windows. The cell was also designed so that the substrate stand with independent temperature control (Ogden, 1/4" Mighty Watt cartridge heater) could be easily removed to facilitate loading of substrates and also to serve as the main section of a controlled-atmosphere cell for obtaining Raman spectra of thin films and surfaces. In use, the entire cell was maintained at constant temperature (±3 °C) with resistance heating tapes and glass cloth insulation. The cell was mounted on a micrometer controlled x-y stage (Newport Research model 405) and vertical stand (Newport
Figure 3.4 Laser photodeposition cell
Research model 410) which allowed for precise positioning of the incident laser radiation on the substrate. Supply and effluent gas lines were maintained at constant temperature with resistance heating tapes. Evacuation of the deposition cell was accomplished with a liquid nitrogen trapped mechanical vacuum pump (Welch model 1402). Cell pressure was monitored with a thermocouple gauge (Granville-Philips series 260 pressure controller) during evacuation and with a capacitance manometer (Datametrics model 570A 1000 torr sensor, model 1173 analog readout) during depositions.

3.1.1.4 Laser and optics system An excimer laser (Lambda Physik EMG 102 MSC) operating at 193 nm was used to provide pulsed incoherent laser light. Excimer gases used were argon (99.995%, Airco), fluorine (99.9%, 5% in helium 99.995%, Spectra Gases), and helium (99.995%, Airco). Laser power and pulse intensity were monitored with a 2" volume absorbing disk calorimeter with an analog readout (Scientech model 38-0203, and model 364 readout). For perpendicular incidence experiments, the laser beam passed through a thin aluminum pattern mask, an optional 50% transmission 1/8" quartz attenuating disk, and through the front window of the laser deposition cell.

For parallel beam experiments, two front-coated aluminum mirrors (Harrick Scientific Corp., #MOP-116 reflectivity 85% at 200 nm) were inserted in the beam path to direct the beam through a side window as shown in Figure 3.5. Parallel
Figure 3.5 Laser photodeposition optics layout and beam path
depositions were performed using a rectangular (~1 mm x 6 mm) mask to define the beam profile. This beam was directed over the surface of the substrate with the 6 mm axis normal to the surface.

The laser, optical components, and laser deposition cell were mounted on a portable table designed to put the laser beam at a convenient height for possible future in situ Raman or fluorescence spectroscopy experiments.

3.1.1.5 Safety  Due to the hazardous nature of both the excimer laser gases and organometallic reactants a special ventilation system was designed. Hazardous excimer gas cylinders were contained inside a ventilated gas cabinet while dedicated ventilation ducts were employed for the laser head and deposition cell region of the experiment table. In addition the gas feed system was located close to a fume hood. Eye protection for 193 nm radiation (Fred Reed Optical model FR2-PL-GG9-GBS) was employed at all times when using the excimer laser.

3.1.1.6 Mass spectrometer system  Reactant concentrations were monitored in situ using a mass spectrometer system and sampling probe. The mass spectrometer system consisted of a quadrupole mass analyzer probe and controller (UTI 100C) and a data acquisition system (Digital Equipment Corp. PDP-11/23, "in-house" Fortran control programs). Due to the insufficient graphics and data manipulation capabilities of the Fortran controlling programs, an
additional Fortran program was written to transform data files to ASCII text files which were transferred to a spreadsheet program on a personal computer for further analysis and output. The sampling probe consisted of a long, 22 gauge, stainless steel syringe needle welded to 1/16" stainless steel tubing which led to the mass spectrometer. By cutting the tip of the needle with wire cutters the opening could be made small enough to sample gas at atmospheric pressure at an acceptable rate (estimated at a few cm³/min). The probe was inserted into the laser deposition cell through a septum (Altech Ultra-sep R®) and the tip positioned at various points on or near the substrate as shown in Figure 3.4.

3.1.2 Procedures

The following section describes the normal conditions, necessary calibrations, and routine procedures used for typical laser deposition experiments.

3.1.2.1 Reactant supply Molybdenum hexacarbonyl (Alfa Products, 99%) was used as the organometallic source molecule in all gas phase laser depositions reported in this work. The saturator was maintained at 40-50 °C and all gas lines and surfaces which contacted reactant gas were maintained at 60-70 °C. The saturator performance was tested by weighing solid Mo(CO)₆ which was collected in a Pyrex®
tube immersed in liquid nitrogen at the effluent return connection of the gas feed rack. This procedure ensured that material lost in the system anywhere before the scavenger reactor would be detected. The amount of material collected was found to be within 10% of that expected from the vapor pressure correlation [117] shown in Equation 3.1.

\[ \log_{10}(P_{\text{vap}}) = 11.406 - \frac{3654}{T} \quad \text{P}_{\text{vap}} \text{ in torr, } T \text{ in } ^\circ\text{K} \quad (\text{Eq. 3.1}) \]

The variation was due to the large changes in vapor pressure as a result of small variations in the saturator temperature. The vapor pressure of Mo(CO)\(_6\) at 50 °C was determined to be 1.25 torr, in excellent agreement with Equation 3.1. Therefore Equation 3.1 was used to calculate saturator stream concentrations at temperatures near 50 °C.

The laser deposition cell was designed to operate at gas velocities in the range of a few cm/s. Satisfactory performance for preventing window fouling at 1 atmosphere total pressure was found for window flush and reactant channel flowrates of 1500 standard cubic centimeters per minute (sccm) and 100 sccm, respectively. These flowrates were used for all laser deposition experiments.

3.1.2.2 Substrate preparation Silicon substrates were prepared by cleaving Si(100) (Aurel, p-type 30-50 ohm-cm) or Si(111) (n-type 4-9 ohm-cm) wafers into 11 mm squares. Before loading onto the substrate stand, the silicon
substrates were cleaned with (sequentially) 1,1,1-trichloroethane, acetone, and methanol (Baker MOS grade), and rinsed with deionized water. Silicon substrates were then oxide etched using buffered hydrofluoric acid (hydrofluoric acid and ammonium fluoride, Baker MOS grade), rinsed thoroughly with deionized water, blown dry in an argon stream, and loaded onto the substrate stand.

3.1.2.3 Loading and calibration After attaching the substrate stand the cell was subjected to 4-5 repetitions of evacuation to \(10^{-1}\) torr and backfilling with helium to 1000 torr then flushed at window flush only flowrates for at least 10 minutes. During this time the temperature of the substrate was raised to the desired temperature in the range 60-120 °C.

The reactant streams were then adjusted to values that gave the desired concentrations while resulting in a total flowrate of 100 sccm. The normal Mo(CO)₆ concentration was 140 ppm (0.1 torr) while oxygen concentrations were 0-30%. Concentrations of Mo(CO)₆ at various positions inside the laser deposition cell were monitored in situ using the mass spectrometer probe. Calibrations were based on the direct proportionality observed between the m/e 98 ion current and calculated reactant concentration. Molybdenum (m/e 98) and oxygen (m/e 32) ion currents were observed with the mass spectrometer sampling needle inside the reactant channel. The needle was then positioned on the substrate about 0.2 mm
downstream of the position where a spot was to be deposited. Reactant ratios were adjusted to give the same ion currents observed inside the undiluted reactant channel. After depositing a spot, the cell was moved to a new position and conditions were changed and allowed to equilibrate before depositing the next spot.

3.1.2.4 Laser operation  
Beam inhomogeneity is a common problem in excimer lasers. For this reason care was taken to insure that the 1 mm diameter spot used for deposition did not contain any small "dead spots". This was accomplished by visually inspecting the initial pattern of material removed from a target of white paper coated with nonwhite material or nonpenetrating ink during or after exposure to laser pulses. Certain magazine covers worked well. The laser was operated most commonly at repetition rates of 8 Hz and total powers of 90-550 mW, corresponding to pulse intensities of 10-60 mJ/cm². Depositions were performed using 1000 to 15000 pulses.

3.1.2.5 Shutdown procedures  
After depositions were completed the reactant gas flow was stopped and the cell and lines were flushed for more than 30 minutes while the substrate stand cooled. The substrate stand was capped with the quartz Raman cell cap and flushed with more than 200 volumes of helium. An alternate procedure was to remove the substrate and store it in a capped vial filled with helium in a desiccator.
3.1.2.6 System maintenance

Over time, the front window of the photodeposition cell would begin to show faint spot images. These fouled areas of the window were avoided during subsequent experiments. Eventually the front window was replaced by tapping it out or shattering it from the inside with a screwdriver. The bonding surface was scraped and cleaned and a new window was cemented in. Exposing the mass spectrometer to molybdenum hexacarbonyl and oxygen led to small amounts of molybdenum oxide buildup on the electron reflector cage which resulted in an increase in the background m/e 16 signal.

3.2 Preparation of Solid Compounds

3.2.1 Molybdenum Oxides

Orthorhombic (γ) Mo₄O₁₁ was prepared by two techniques. In the first procedure, stoichiometric amounts of MoO₃ (Alfa Products, 99%) (dried 1 day 100 °C in air) and MoO₂ (Alfa 99%) were ground with an agate mortar and pestle. Approximately 2.5 grams of this gray powder was sealed in an evacuated 8 mm quartz tube. The sample was heated for 18 hrs at 700 °C in a muffle furnace (Linde, model 59545). Alternatively large crystals of monoclinic (η) Mo₄O₁₁ prepared by the temperature gradient flux technique [118] (courtesy of Dr. M. Greenblatt,
Rutgers University) were ground, sealed in a quartz tube and heated for 42 hours at 700 °C.

3.2.2 Alternative Precursors

A wide variety of organometallic and "metallo-organic" (referring to compounds in which the metal is bound to the ligands through oxygen) exist. However, very little is known about the volatility and photochemistry of these compounds. A few compounds which had reasonable probabilities of possessing the necessary characteristics of a good metal or metal oxide source for laser deposition were synthesized as described below. All syntheses were performed in a fume hood using a Schlenk type manifold, Pyrex® glassware and Teflon® magnetic stirring bars.

3.2.2.1 \( \text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \) Molybdenum trifluoroacetate dimer (TFAMo) was prepared by ligand exchange from molybdenum acetate dimer using the method of Cotton and Norman [98].

Approximately 28 grams of molybdenum acetate dimer, \( \text{Mo}_2(\text{CH}_3\text{CO}_2)_4 \), was prepared as follows [119]. Dry nitrogen was bubbled through a solution of 300 ml acetic acid (Baker, MOS grade) and 30 ml \( \text{N}_2\text{N}'\text{N}',\text{N}''\)-tetramethyl ethylene diamine (Aldrich Chemical Co.). After 10 minutes, 40 grams of \( \text{Mo(CO)}_6 \) (Alfa 99%) was added. The resulting solution was refluxed under nitrogen with stirring for approximately 24 hrs. During the first 12 hours it was necessary to
continuously scrape the Mo(CO)$_5$, which crystallizes in the condenser, down into the reaction flask. The resulting orange solution was allowed to cool and filtered in air. The yellow precipitate was washed with 200 ml absolute ethanol and 30 ml of anhydrous ether (Fisher) and dried in vacuo at room temperature. The bright yellow crystalline powder was stored under nitrogen. A solution containing 4.0 g of Mo$_2$(CH$_3$CO$_2$)$_4$, 6 ml trifluoroacetic acid (Aldrich), and 60 ml of trifluoroacetic anhydride was heated to boiling, allowed to cool to room temperature and cooled to -10 °C for 1 hour. After filtering the solution (in air), the intense yellow crystals were washed with pentane, dried in vacuo at room temperature, and stored under nitrogen. The yield for the first crop was approximately 3 grams. A second crop of crystals was also collected by concentrating the solution and additional cooling.

3.2.2.2 Mo(C$_3$H$_5$)$_4$ Tetra-allylmolybdenum was synthesized from tetrachlorobis(tetrahydrofuran) - molybdenum(IV), (MoCl$_4$(THF)$_2$), according to the method of Benn et al. [95]. All procedures were carried out under nitrogen. First MoCl$_4$(THF)$_2$ was prepared as follows [120]. Tetrahydrofuran (THF) (100 ml, freshly distilled from sodium benzophenone ketyl) was added by syringe under nitrogen to a flask containing 25 g of bisacetonitrile(tetrachloro - molybdenum)(IV), MoCl$_4$(CH$_3$CN)$_2$ (Aldrich Chemical Co.) and the solution was stirred for 2 hours. The resulting orange-brown
solid suspended in green liquid was filtered under nitrogen, washed with 30 ml THF and dried \textit{in vacuo} at room temperature. The crystalline orange-brown solid (approximately 20 g) was stored under argon. Then 7.6 g of MoCl$_4$(thf)$_2$ was added slowly, at room temperature, to a stirred solution (263 ml) of 0.38 M allylmagnesium bromide in ether which was comprised of 100 ml 1.0 M allylmagnesium bromide in ether (Aldrich Chemical Co.) diluted with 163 ml ether (freshly distilled from sodium benzophenone ketyl). After cooling to 0 °C and stirring for 12 hours, the dark green solution was extracted with approximately 100 ml of pentane (freshly distilled from calcium hydride). Air was bubbled through the solution to decompose traces of the intensely colored "dimeric" by-product (Mo$_2$(C$_3$H$_5$)$_4$) and the solution was filtered through Celite$. After concentrating the resulting yellow solution under vacuum, cooling and filtering under nitrogen, recrystallizing from pentane, and drying at room temperature under vacuum, approximately 1 gram of yellow crystalline solid was isolated.

3.2.2.3 Mo$_2$(C$_3$H$_5$)$_4$ Attempts were made to prepare and isolate tetra-µ-allyldimolybdenum by the method of Candlin and Thomas [93]. Although the reaction proceeded as expected, the extreme air-sensitivity of the intense dark green product led to its decomposition during the final \textit{in vacuo} concentration step.
3.2.2.4 \( \text{MoO}_2(C_5\text{HF}_6\text{O}_2)_2 \) and \( \text{Mo}_2\text{O}_3(C_5\text{HF}_6\text{O}_2)_4 \)

Attempts were made to synthesize and isolate dioxobis-(hexafluoro-acetylacetonate)-molybdenum (VI) or the recently reported \([104]\) \( \mu \)-oxo-dioxotetrakis(hexafluoroacetylacetonate)-dimolybdenum (V). First the nonfluorinated dioxobis(acetylacetonate)-molybdenum (VI) (\( \text{MoO}_2(C_5\text{H}_7\text{O}_2)_2 \)) was prepared by the method of Jones \([121]\). In air, ammonium paramolybdate, \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O} \) (Fisher Scientific), (2.71 g) was dissolved in 15-20 ml of deionized water. Acetylacetone (acacH) (Aldrich Chemical Co.) (3.45 ml, 10% excess) was added to the solution with stirring. After the acacH dissolved, the pH was adjusted to 3.5 by the dropwise addition of 10% \( \text{HNO}_3 \) (Fisher Reagent Grade). A pale yellow precipitate formed immediately. After standing for 1 hour the solution was filtered and the precipitate (1.7 grams) dried in air. Attempts to form the fluorinated compound by substituting hexafluoroacetylacetone (hfacacH) (Aldrich Chemical Co.) for acacH in the aqueous synthesis failed and resulted only in the formation of a highly crystalline white (transparent) compound believed (from Raman and FTIR characterization) to be 1,5-hexafluoropentane-diol. A solution of \( \text{MoO}_2(C_5\text{H}_7\text{O}_2)_2 \) (0.51 g) and hfacacH (5 ml) was prepared and slowly heated under a nitrogen atmosphere. At 54 °C the solid had completely dissolved to leave a golden-yellow solution and a small amount of grey precipitate. The solution was allowed to cool and the clear supernatant was
transferred with a cannula, under nitrogen, to a dry nitrogen filled test tube. After two days at room temperature, the solution was very dark red-brown (the color reported in [104]). Sealed capillary samples of this solution were prepared in an argon glovebox and analyzed by Raman spectroscopy before and after the color change. An attempt to recover solid product by cooling for 2 weeks was unsuccessful. Upon concentration under vacuum the solid apparently re-reacted with the remaining (less volatile) acacH.

3.3 Raman Spectroscopy

3.3.1 Apparatus

3.3.1.1 Spectrometer system  Raman spectroscopy was performed using the system described below. An argon ion laser operating at 514 nm (Spectra Physics model 164) was used to illuminate samples in a variety of holders discussed in later paragraphs. Raman scattered radiation was collected and dispersed using a triple monochromator (Spex Triplemate) fitted with standard collection optics (Spex model 1459 UV/VIS sample illuminator) and spectrograph stage gratings of 600 and 1200 grooves/mm. The dispersed radiation was focused on a multichannel photodiode array detector (EG+G PARC model 1420) which was controlled by an optical multichannel
analyzer system (EG+G model 1218 detector controller and model 1215 console). An additional cylindrical lens (Esco Products, Suprasil, 1.25" diam., 3" focal length) was employed at the exit of the spectrograph stage in order to focus the rectangular radiation pattern onto the linear photodiode array [122]. Extensive modifications to the photodiode array detector and controller were performed to enhance performance and are described in detail below.

3.3.1.2 Detector enhancements Due to the minute quantity of material sampled, thin films and surfaces produce extremely weak Raman signals and therefore require long collection times. Sensitivity of the technique can be increased by reducing the noise level or by increasing the strength of the signal. Characteristic magnitudes of noise from various sources in the detector system dictate that the minimum noise level is obtained for one long scan as opposed to the sum of many short scans. The maximum possible length of a scan is limited by the time necessary to saturate the dynamic range of the detector/collection system. The total signal observed by the collection system is comprised of the sum of the desired signal generated as a result of collection of photons, the background signal due to carriers randomly generated in the electronic materials, and a DC offset. By reducing the background count rate and DC offset, the portion of the system’s dynamic range available for the desired signal can be maximized. Thermally generated carriers are a
major source of background signal and the generation rate is exponentially dependent on temperature.

The photodiode array is cooled by a thermoelectric device (Peltier effect). Operating against room temperature air, the electronics of the system are capable of cooling the photodiode array to approximately -28 °C. A coolant refrigeration/recirculation system (Lauda model RMS-6) was employed to provide a more efficient heat sink for the thermoelectric cooler. Modifications were made to the controller electronics so that the thermoelectric cooling device would run "flat out" (against zero resistance in the balancing portion of the bridge circuit). With these modifications it was possible to reach -40 °C, the minimum safe operation temperature (due to thermal stresses on components) of the detector.

The entire detector housing was insulated both for isolation from room temperature variations and to further reduce thermal electronic noise by cooling all of the electronic components in the detector. At this low temperature it is imperative to purge the detector with dry gas to prevent the formation of ice in the detector. As a result of these modifications, the resulting thermistor temperature and background rate were reduced from the initial -3 °C and 2500 counts/s to -40 °C and 14 counts/s (a factor of 175). The corresponding maximum single scan collection time (dynamic range approximately $2^{14}$ counts) was increased from 7
seconds to 20 minutes. For a given collection time, the reduction in noise level was actually significantly more than 175 times due to the elimination of the need for a large number of short scans. Subtraction of two 1024 second background scans resulted in peak-to-peak noise of approximately 10-20 counts allowing the detection of signals on the order of 30-40 counts or approximately 0.04 counts/s.

3.3.1.3 Raman cell design A special cell was designed to obtain Raman spectra of thin films and materials of questionable air sensitivity (as pellets). Finding the Raman signal of a surface or thin film is an extremely difficult and time consuming operation. Therefore the cell and positioning system were designed to give repeatable positioning and to minimize the need for realignment. The cell, as shown in Figure 3.6, is comprised of a temperature controlled substrate stand mounted in an o-ring compression fitting (Cajon Ultra-torr®, 1" adapter with Viton® o-ring) base modified with valves (Whitey) for purging, supplying a controlled atmosphere, or evacuating the cell. The cell is oriented in the Raman collection optics such that the angle of incidence of the polarized laser beam is at approximately 60° to the surface normal. A unique quartz cap which seals the cell was fabricated from a 1" diameter quartz tube. Flat quartz windows were attached with low vapor pressure cement (Torr-Seal®) at angles such that the incident and collected radiation passed through flat surfaces normal to the light
Figure 3.6  Controlled atmosphere, controlled surface temperature cell for Raman spectroscopy of thin films and surfaces
path thereby minimizing optical distortions and sensitivity to small changes in window orientation and position. A micrometer controlled x-y table (Newport Corp., model 400) was employed to translate the cell parallel to the sample surface such that the surface of the substrate always remained at the focus of the incident laser and spectrometer collection optics. This apparatus is shown in Figure 3.7. Raman spectra could thus be obtained at various positions on a substrate with virtually no need for realignment. The attitude of the cell with respect to the incident beam and collection optics could be adjusted around two axes by rotating the pivot arm assemble or by repositioning the entire stand around the axis of the incident beam. A vertical stand (Newport Corp. model 410) and micrometer controlled translation stages (Newport Corp., models 430-1 and 400) provided precise and repeatable positioning of the cell.

3.3.1.4 Other sampling techniques Three techniques were used to obtain Raman spectra of solid materials. Compounds with strong Raman scattering characteristics, such as MoO₃, Mo(CO)₆, and Mo₂(CF₃CO₂)₄, were studied by sealing a small quantity of material in a 1 mm Pyrex® capillary tube. For air sensitive compounds, such as Mo(C₃H₅)₄, the capillaries were evacuated, or evacuated and filled with an inert atmosphere before sealing in an oxygen gas flame using the capillary sealing apparatus shown in Figure 3.8. Solids
Figure 3.7 Positioning stand for thin film Raman cell
Figure 3.8 Capillary sealing apparatus
with weaker scattering characteristics, such as MoO₂ and Mo₄O₁₁, were ground with potassium bromide (KBr) (Fisher Scientific) and pressed (approximately 15000 psi) into pellets and studied using two 90° scattering techniques. By using a small piece of pressure sensitive tape on the back side, pellets could be mounted on the substrate stand of the controlled atmosphere Raman cell and studied under an inert atmosphere. A similar method was employed to obtain spectra of the large crystals of monoclinic Mo₄O₁₁ in which a crystal was cemented onto a silicon substrate. In the second technique, pellets were studied using a holder which spun the pellet at approximately 1000 rpm to minimize any possible photolytic or thermal decomposition.

3.3.2 Procedures

In all cases, strict precautionary procedures were followed to insure that the integrity of the original samples was retained during Raman studies. Laser induced thermal or photolytic reactions with air were prevented by controlling the atmosphere in contact with the sample during Raman experiments. The controlled atmosphere cell was flushed with at least 500 cell volumes of helium before exposure to the incident laser and was continually purged for the remainder of the experiment. Every sample was first subjected to very low incident laser power (20 mW at the laser, approximately
10 mW at the sample) at the expense of signal quality to minimize the possibility of thermal or photolytic decomposition. Laser power was then increased incrementally while the Raman spectrum of the sample was monitored. Any changes observed in the Raman spectrum during this procedure were noted and measurements on subsequent similar samples were limited to laser powers well below these thresholds.

Typical scan parameters used in the Raman analyses are outlined below. Variations for specific sampling techniques are noted. Raman spectra were obtained using a 600 groove/mm grating which resulted in a 1600 cm\(^{-1}\) field of view with 8 cm\(^{-1}\) resolution or a 1200 groove/mm grating which led to a 900 cm\(^{-1}\) field of view with 4 cm\(^{-1}\) resolution. A single scan, typically 512 s in length, was used in most cases. For samples studied inside the controlled atmosphere cell, the laser power was 100 mW at the source (approximately 50 mW at the sample). Raman signals for deposited materials and mounted crystals were located by aligning on the silicon substrate and then translating the cell to position the desired deposit or crystal at the focal point of the instrument. Lower powers were used for the pellet spinning apparatus due to the lack of a controlled atmosphere. Capillaries of the strong Raman scatterers were studied with low powers (20-100 mW) and scan times as short as 0.25 seconds. In certain cases high powers (200 mW - 1.6 W) were
used in attempts to intentionally induce a reaction or decomposition.

3.4 Other Characterization Methods

The characterization techniques below were also used in this research to analyze laser deposited material and bulk solids. Identities of some of the bulk compounds were verified by powder diffraction (Siemens D500 X-ray diffractometer, Cu-K$_\alpha$ radiation). Ellipsometry (Gaertner Scientific Corp., 632.8 nm, 70° angle of incidence) was used to measure the thickness and index of refraction of laser deposited films. Scanning electron microscopy (SEM) (JEOL JSM-840A, 10 keV) was used to study the surface morphology of the laser deposited films as well as to estimate the thickness of the deposit in cross section. Energy dispersive X-ray spectroscopy (EDS) (Kevex Delta V microanalyzer used with the above SEM at 10 or 4 keV) was utilized to determine the atomic constituents in the laser deposited films. Contamination levels of the films was also studied with Auger electron spectroscopy (AES) (Perkin Elmer PHI 600 Scanning Auger Microprobe). Crystallinity of a laser deposited film was studied using an X-ray Read (wide film Debye-Scherrer) camera and Cu-K$_\alpha$ radiation. The silicon substrate was oriented at 11.5° with respect to the incident radiation. A
phosphor screen (MCI Optonix "Detail Speed") was used in conjunction with film (Kodak SB) for a 24 hour exposure.
4 RESULTS AND DISCUSSION: CHARACTERIZATION AND EVALUATION OF SOLID COMPOUNDS

This chapter contains the results and discussion of the analyses performed on the solid molybdenum compounds used in this work. In order to recognize and identify compounds which might be formed in the laser deposited films, it was necessary to have standards with which comparisons could be made. The results of the characterization of these molybdenum-containing standards are described in the first section of this chapter. Although Mo(CO)$_6$ was ultimately used as the source material for the UV laser depositions performed in this work, other prospective source molecules which were previously uninvestigated with respect to their suitability for laser deposition processes were prepared and evaluated. The results of the characterization and evaluation of these compounds are presented in the second section of this chapter.
4.1 Characterization of Molybdenum-Containing Standards

4.1.1 X-Ray Powder Diffraction

The observed X-ray powder diffraction pattern for MoO$_2$ is shown in Figure 4.1 and identically matches that reported in the literature [123] except for a small amount of metallic molybdenum (cubic) in the MoO$_2$. Patterns observed for orthorhombic and monoclinic Mo$_4$O$_{11}$ are shown in Figures 4.2 and 4.3. The observed peak positions correspond identically with those reported in the literature while inconsistencies in observed intensities are due to variations in the X-ray sample preparation, such as particle size and preferential orientation of the particles on the plastic adhesive tape.

4.1.2 Raman Spectroscopy of Solids

Raman spectroscopy was also used to characterize the molybdenum containing standards. In addition to the normal Raman characterization techniques employed, some materials were subjected to conditions during Raman analysis (non-inert atmospheres and/or high incident laser powers) with the intent of inducing chemical reactions. These reactions were subsequently monitored in situ.
Figure 4.1  X-ray powder diffraction pattern of MoO$_2$. 
Figure 4.2  X-ray powder diffraction pattern of \( \gamma-\text{Mo}_4\text{O}_{11} \)
Figure 4.3 X-ray powder diffraction pattern of $\eta$-Mo$_4$O$_{11}$
4.1.2.1 $\alpha$-MoO$_3$. Crystalline molybdenum trioxide ($\alpha$-MoO$_3$) is an excellent Raman scatterer and the spectrum shown in Figure 4.4 was easily obtained by the sealed capillary technique. In fact, at the 5 cm$^{-1}$ resolution used and the lower limit of incident laser power (20 mW at the laser, approximately 10 mW at the sample), the 821 cm$^{-1}$ peak was capable of saturating the dynamic range of the detector in approximately 0.25 seconds. For comparison with other compounds discussed later, the signal for the 821 cm$^{-1}$ peak resulting from 100 mW incident radiation on a pellet (concentration about 20 % in KBr) was roughly $1 \times 10^5$ counts/s. The low wavenumber region of the spectrum is shown in the inset of Figure 4.4. No induced reactions were observed for the $\alpha$-MoO$_3$. This might, however, be due to the fact that the possible resulting products, such as reduced molybdenum oxides, are relatively weak Raman scatterers and were obscured by the strong $\alpha$-MoO$_3$ spectrum.

4.1.2.2 MoO$_2$. Conversely, crystalline MoO$_2$ is a relatively poor Raman scatterer and the spectrum shown in Figure 4.5 necessitated the use of pellets, 90° scattering, and the exclusion of air by flushing the controlled atmosphere Raman cell with helium. For comparison, at the test conditions (pellet 20% in KBr, 100 mW), the 743 cm$^{-1}$ peak of MoO$_2$ gave about 2 counts/sec. In a helium atmosphere, no changes in the spectrum were observed at low powers while small shifts in the 200 cm$^{-1}$ region peaks.
Figure 4.4 Raman spectrum of solid $\alpha$-MoO$_3$
Figure 4.5 Raman spectrum of solid MoO$_2$. 
attributed to changes in temperature were observed with increasing incident laser power. With an air or oxygen atmosphere, MoO\textsubscript{2} was found to undergo oxidation to \(\alpha\)-MoO\textsubscript{3} as a result of incident laser radiation at 514 nm. This phenomenon was observed both for pellets as well as air-filled capillaries. At 100 mW incident power, \(\alpha\)-MoO\textsubscript{3} peaks could be detected after approximately 5-10 minutes, whereas at powers above 600-700 mW the formation (observation) of \(\alpha\)-MoO\textsubscript{3} occurred faster than minimum scan length of the detector system (0.016 seconds). No intermediate oxides (MoO\(_x\) where 2 < x <3) were observed during the oxidation of MoO\textsubscript{2} to \(\alpha\)-MoO\textsubscript{3}. It was not determined whether this particular oxidation was induced photolytically or thermally although the thermal oxidation of MoO\textsubscript{2} to \(\alpha\)-MoO\textsubscript{3} is well known [124]. Attempts to observe the low wavenumber Raman spectrum of MoO\textsubscript{2} were thwarted by the overwhelming Rayleigh scattering below 180 cm\(^{-1}\).

4.1.2.3 \(\text{Mo}_4\text{O}_{11}\) Both orthorhombic (\(\gamma\)) and monoclinic (\(\eta\)) \(\text{Mo}_4\text{O}_{11}\) were observed to be poor Raman scatterers similar in strength to MoO\textsubscript{2}. The spectra of \(\gamma\)- and \(\eta\)-Mo\(_4\)O\(_{11}\) shown in Figures 4.6 and 4.7 were obtained from pellets in the controlled atmosphere Raman cell with helium flushing and a power of 100 mW measured at the laser. Raman spectra obtained previously by this group [125] were of lower quality (signal-to-noise) and were limited to the spectral range above 400 cm\(^{-1}\) below which Rayleigh scattering
Figure 4.6 Raman spectrum of solid $\gamma$-Mo$_4$O$_{11}$
Figure 4.7 Raman spectrum of solid $\eta \text{Mo}_4\text{O}_{11}$
overwhelmed the Raman spectrum. In the 400-1000 cm\(^{-1}\) range peak positions of the spectra obtained in this work match with those of the earlier work and relative intensities follow essentially the same trends. The spectra presented in Figures 4.7 and 4.8 also include the previously unreported spectral region below 400 cm\(^{-1}\).

A single crystal of monoclinic Mo\(_4\)O\(_{11}\) was studied with the laser impinging on the bc plane ((100) face) and approximately parallel to the b-axis at 60\(^\circ\) from the surface normal as shown in Figure 4.8. Helium flushing was used to exclude oxygen from the cell. Increasing the laser power from 100 to 400 mW with air in the cell did not cause any noticeable changes in the spectrum. Rayleigh scattering overwhelmed the Raman signal below approximately 170 cm\(^{-1}\).

4.1.2.4 \(\beta\)-MoO\(_3\) In light of the recent discussions of the newly discovered \(\beta\)-phase MoO\(_3\) [65,66] and its formation by the oxidation of \(\gamma\)-Mo\(_4\)O\(_{11}\) [67], attempts were made to form and observe \(\beta\)-MoO\(_3\). Crystalline powders of \(\gamma\)-Mo\(_4\)O\(_{11}\), \(\eta\)-Mo\(_4\)O\(_{11}\), and MoO\(_2\) were each sealed in air filled capillaries and subjected to increasing incident laser powers while simultaneously monitoring their Raman spectra. Surprisingly, \(\beta\)-MoO\(_3\) was formed in all three cases. At 50 mW none of the samples exhibited any detectable Raman scattering over the fluorescence generated from the Pyrex\textsuperscript{\textregistered} capillaries. Using a laser power of 200 mW, a sample of \(\eta\)-Mo\(_4\)O\(_{11}\) showed a strong \(\beta\)-MoO\(_3\) spectrum 10 seconds after the
Figure 4.8 Raman spectrum of single crystal \( \eta-\text{Mo}_4\text{O}_{11} \) with the incident beam at \(-60^\circ\) to the surface normal of the bc plane and \(90^\circ\) scattering collection.
onset of laser incidence. Shown in Figure 4.9 is the Raman spectrum of a sample of $\gamma$-Mo$_4$O$_{11}$ after 32 seconds of laser (200 mW) exposure. Unexpectedly, $\beta$-MoO$_3$ was even formed from MoO$_2$ although significantly higher laser power (500 mW) was needed to induce the reaction. The spectrum shown in Figure 4.9 is representative of the spectra observed for each of the three transformations observed. In each case the $\beta$-MoO$_3$ signal grew with time and eventually stopped increasing. Increasing the laser power at this point led to the formation of more $\beta$-MoO$_3$ and/or some $\alpha$-MoO$_3$, as also seen in Figure 4.9. Further increases in the laser power ultimately led to the complete conversion of the $\beta$-MoO$_3$ to $\alpha$-MoO$_3$. Only $\alpha$-MoO$_3$ was observed when previously unexposed samples were subjected to high laser powers (> 800 mW) from the start. The method which led to the formation of $\beta$-MoO$_3$ with the smallest amount of coexisting $\alpha$-MoO$_3$ was the same for all three starting compounds. While monitoring the Raman spectrum, the laser power was slowly increased until the 850 cm$^{-1}$ peak of $\beta$-MoO$_3$ was observed. After the signal stopped increasing, the laser power was increased again. This technique produced spectra with very little evidence of $\alpha$-MoO$_3$ until further increases in the laser power initiated the transformation of $\beta$-MoO$_3$ to $\alpha$-MoO$_3$. 
Figure 4.9 Raman spectrum of $\beta$-MoO$_3$ formed by 514 nm laser incidence on an air-filled capillary of $\gamma$-Mo$_4$O$_{11}$
4.2 Discussion of Results: Molybdenum-Containing Standards

4.2.1 Comparison of Raman Spectra

Table 4.1 presents a comparison of the Raman spectra of the molybdenum oxides studied in this work. On comparing the Raman spectra of the various molybdenum oxides, vibrational frequencies characteristic of specific oxidation states and/or coordination geometries can be identified. The unique slab structures of the Mo$^{V}$ compounds provide an interesting system which can be described to some degree as a collection of $\beta$-MoO$_{3}$ slabs and tetrahedral Mo$^{4+}$ (MoO$_{2}$) units. In fact the Raman spectra of the Mo$^{V}$ appear to be comprised of the superposition of peaks characteristic of the corner shared octahedra of $\beta$-MoO$_{3}$ and of peaks characteristic of Mo$^{4+}$ in MoO$_{2}$. In addition, the Mo$_{4}^{IV}$ compounds can aid in assigning vibrational frequencies in $\beta$-MoO$_{3}$, MoO$_{2}$ and possibly $\alpha$-MoO$_{3}$.

The corner shared octahedra slab structure of $\beta$-MoO$_{3}$ is obviously responsible for the three main peaks of the Mo$_{4}^{IV}$ spectra at 783-793, 831-845, and 906-911 cm$^{-1}$. These peaks correspond with the 775, 850, and 900 cm$^{-1}$ peaks of $\beta$-MoO$_{3}$. Since $\beta$-MoO$_{3}$ is comprised entirely of (albeit distorted) corner shared octahedra, it seems reasonable to assign the intense 821 cm$^{-1}$ peak of $\alpha$-MoO$_{3}$ to a similar type of
Table 4.1 Comparison of molybdenum oxide Raman spectra

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(a) this work, observed in thin film
(b) Garcia and McCarron [66]
vibration resulting from doubly coordinated oxygen Mo-O-Mo bonds. This assignment is in agreement with previous investigations [126] but differs from that of Py et al. [127,128]. The peaks of $\gamma$-Mo$_4$O$_{11}$ at 834 and 845 cm$^{-1}$ could be result of the alternating orientations of the octahedral MoO$_3$ "slabs". In $\eta$-Mo$_4$O$_{11}$ and $\beta$-MoO$_3$, these "slabs" are all aligned in the same direction and have only single peaks near this wavelength.

Vibrations which are characteristic of tetrahedral and/or Mo$^{4+}$ can be seen in the 727-743, 364-377, 223-229, and 183-205 cm$^{-1}$ regions. As shown in Table 3.1, MoO$_2$ and both Mo$_4$O$_{11}$ phases exhibit peaks in each of these regions. The Mo$_4$O$_{11}$ compounds exhibit a strong peak at 183-185 cm$^{-1}$ which is believed to correspond to the strong 205 cm$^{-1}$ peak observed in MoO$_2$. The position of the 205 cm$^{-1}$ peak of MoO$_2$ was observed to shift significantly as a function of temperature while the 183-185 cm$^{-1}$ peaks of the Mo$_4$O$_{11}$ seemed less influenced by temperature.

The single crystal Raman spectrum of $\eta$-Mo$_4$O$_{11}$ shows changes in relative peak intensities when compared to the ground (randomly oriented) sample. Although further study is beyond the scope of this work, it is apparent that Raman spectroscopy of various orientations of Mo$_4$O$_{11}$ single crystals could contribute significantly to the current understanding of the structure, symmetry, and vibrational modes of a number of molybdenum oxides.
4.2.2 Formation of $\beta$-MoO$_3$ "intermediate".

The formation of $\beta$-MoO$_3$ by the thermal oxidation of $\gamma$-MoO$_3$ has recently been reported by Svensson and Kihlborg [67]. The observation of the formation of $\beta$-MoO$_3$ during the Raman studies in this work seems to indicate that $\beta$-MoO$_3$ can form not only from both $\gamma$- and $\eta$-MoO$_3$, but also from solid MoO$_2$. It is very possible that the $\beta$-MoO$_3$ observed in this work was formed as a result of the oxidation of the surface of the reduced oxide particles. $\beta$-MoO$_3$ is probably an excellent Raman scatterer and it is possible that the observed signals were due to a very small quantity of material.

It is not known at this time whether the oxidation processes leading to the formation of $\beta$-MoO$_3$ were solely a result of thermal mechanisms. It is possible that the 514 nm laser radiation induced some photolytic process. It is also impossible to rule out involvement of the glass capillary surface. It is possible that MoO$_3$ species are inherently mobile (see Chapter 5, Discussion) on SiO$_2$ surfaces and consequently can form crystallites.
4.3 Characterization and Evaluation of Precursors

4.3.1 Mo(CO)_6

Molybdenum hexacarbonyl is known to be a thermally stable compound with measurable vapor pressure below 100 °C. These properties along with its known photochemical activity made it a prime candidate as a gas phase organometallic source for laser photodeposition experiments. It was found (in this work but not reported here) to be an extremely efficient Raman scatterer with very intense peaks at 104, 407, and 2007 cm\(^{-1}\) [129-132]. The solid (capillary technique) gave rise to strong signals similar in magnitude to MoO_3. By using the surface Raman cell and a silicon substrate, Raman spectra of gas phase Mo(CO)_6 (~.5 torr in He) could also be obtained in the CO vibration (2000 cm\(^{-1}\)) region. If present in the deposited films, the source material would have been relatively easy to detect with the Raman technique. Another interesting phenomenon of molybdenum containing compounds is the isotopic "fingerprint" observable in the mass spectrum beginning at m/e 92 as shown in Figure 4.10. The m/e 98 signal of molybdenum was used to monitor the Mo(CO)_6 concentration during photodeposition experiments as no other molybdenum containing species were ever observed to reach the mass spectrometer for detection. The vapor pressure of Mo(CO)_6
Figure 4.10  Mass spectrum of Mo(CO)$_6$
was given previously in Equation 3.1 and is too high at room temperature to allow the use of Mo(CO)$_6$ as a spin-on solid film precursor because the film would sublimate from the surface too quickly.

4.3.2 $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$

Figures 4.11 and 4.12 show the observed Raman spectra of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$, (TFAMo), and the closely related starting material $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$. The very bright (almost fluorescent) yellow solid, TFAMo, was found to be indefinitely stable under nitrogen at room temperature. No observable decomposition occurred after exposure to air for a period of 2 weeks. This is in contrast to the nonfluorinated $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$ which decomposes over a period of weeks under nitrogen and days in air, changing from bright yellow to brown. In addition, the TFAMo was stable at elevated temperatures during recrystallization and vapor pressure measurements performed by transporting the subliming compound in a helium stream at 180 °C. The vapor pressure data collected in this work are shown as an Arrhenius plot in Figure 4.13. The derived vapor pressure relationship given in Equation 4.1 is in excellent agreement with the

$$\log_{10}(p_{\text{vap}}) = 30.129 - (1.346 \times 10^4)/T \quad (\text{Eq. 4.1})$$
Figure 4.11: Raman spectrum of solid Mo$_2$(C$_3$O$_4$)$_4$. 

Wavenumbers:
- 1248
- 1209
- 1181
- 875
- 743
- 628
- 501
- 395
- 304
- 204
- 190
- 147
- 63
- 1458
Figure 4.12
Raman spectrum of solid No. 2 (CH$_3$CO)$_2$4
Figure 4.13 Arrhenius plot of the vapor pressure of Mo$_2$(CF$_3$CO$_2$)$_4$
relationship derived from previously published [97] data taken in a much higher temperature range by a completely different measurement technique. The slope and intercept calculated from the data in reference [97] were found to be $-1.399 \times 10^4$ and 30.294 respectively. The estimated vapor pressure at 70 °C, $-1 \times 10^{-9}$, was much too low to be used with the apparatus used in this work (valves 70 °C max, cell 120 °C max). In order to transport the same quantity of molybdenum used in this work, the temperature of the apparatus would need to be maintained above 150 °C. The gas phase photofragmentation of $\text{MoO}_2(\text{CH}_3\text{CO}_2)_2$ has been studied by Vaida [99].

The TFAMo was also found to be extremely soluble and stable in methanol and ethanol while slow decomposition was observed over a period of days in acetone. The viscosity of these solutions could be adjusted by the amount of TFAMo dissolved, and consequently, thin films of TFAMo could be applied to a substrate using a wafer spinner. A film prepared on a silicon substrate by this technique was subjected to decomposition by the focused 514 nm laser during in situ Raman spectroscopy in air. The initial spectrum obtained at low power showed only the TFAMo but on increasing the laser power the TFAMo spectrum was transformed and exhibited $\alpha$-MoO$_3$. By translating the substrate, lines of blue-black material were "written" in the thin TFAMo film. No further characterization was done.
If these "written" lines were indeed some molybdenum oxide, the substrate could be "developed" by rinsing with an organic solvent to remove the soluble TFAMo while allowing the insoluble molybdenum oxide "image" to remain on the surface. The desirable handling properties, low vapor pressure, and ability to form MoO₃ indicate that TFAMo is an excellent candidate for laser depositions from thin solid precursor films.

4.3.3 Mo(C₃H₅)₄

Figure 4.14 shows the mass spectrum obtained for the yellow crystalline Mo(C₃H₅)₄ (MW 262 for Mo⁹⁸) synthesized in this work. The parent peaks near m/e 262 contain the molybdenum isotope fingerprint and clearly identify the compound. Loss of allyl ligands is evidenced by the peaks around m/e 221,180,139, and 98 corresponding to a loss of 1, 2, 3, or 4 ligands. These peaks are broadened by the loss of additional hydrogens. The complicated spectrum also shows the loss of various numbers of single carbon units leaving stoichiometries corresponding to the sum of integral numbers of allyl ligands and C₁ or C₂ fragments. A very large peak (not shown) occurred at m/e 41-42 corresponding to the allyl ligand and C₃H₆. Six and five carbon products are also visible around m/e 82 and 68. These fragmentation products comprised of more than one allyl ligand, C₆H₁₀ in
Figure 4.14  Mass spectrum of Mo(C₃H₅)₄
particular, have been observed previously [96] by proton NMR spectroscopy during the UV photolysis of Zr(C$_3$H$_5$)$_4$ which has the same structure as the molybdenum compound studied in this work.

Every peak observed in the 1600-700 cm$^{-1}$ range of the Raman spectrum of Mo(C$_3$H$_5$)$_4$ presented in Figure 4.15 has a corresponding peak at the same position in the published infrared spectrum [93]. The pair of peaks at 1507 and 1475 cm$^{-1}$ are characteristic of trihapto allyl complexes. The peaks between 500 and 300 cm$^{-1}$ are due to Mo-(C$_3$H$_5$) vibrations and are very similar to other metal-allyl complexes such as Rh(C$_3$H$_5$)$_3$ and Ir(C$_3$H$_5$)$_3$ [133] with the exception of the peak at 443 cm$^{-1}$. Comparisons for the region below 300 cm$^{-1}$ were not made due to the lack of published spectra of similar compounds.

Attempts to measure the vapor pressure of Mo(C$_3$H$_5$)$_4$ failed due to the decomposition of the compound on heating to 50 °C in helium. However, some yellow crystalline solid was transferred before the complete decomposition of the source. Based on this and the signal strength during mass spectrometry it is estimated that the vapor pressure of this compound is between that of Mo(CO)$_6$ and TFAMo and closer to Mo(CO)$_6$. No further work was done on this compound due to its untimely decomposition and the difficulty of its preparation.
4.3.4 Fluorinated acetylacetonate molybdenum (Mo$^{5+}$)

Although a fluorinated acetylacetonate molybdenum compound was never isolated, evidence for its formation by the ligand exchange technique was found. Figure 4.16 shows the Raman spectrum obtained by subtracting the solvent hexafluoroacetylacetone from the ligand exchange solution described in Chapter 3. Also shown, in Figure 4.17, for comparison, is the nonfluorinated starting compound MoO$_2$(acac)$_2$. It is believed that the compound observed is the recently reported $^{[104]}$ Mo$_2$O$_3$(C$_5$HF$_6$O$_2$)$_4$. The C=O stretch at 1554 cm$^{-1}$, as well as the peaks at 1354, 1146, 1106, 738 cm$^{-1}$ peaks correspond very well to ligand vibrations of other metal chelate hfacac compounds $^{[105,134]}$. A vibration of Mo-O single bonds is seen at 460 cm$^{-1}$ while the peak at 955 cm$^{-1}$ is attributed to Mo=O both of which are in good agreement with the nonfluorinated oxo-bridged Mo$_2$O$_3$(acac)$_4$ reported previously $^{[103]}$. 
Figure 4.16 Raman spectrum of MoO$_2$(C$_5$H$_7$O$_2$)$_2$ in hexafluoroacetylacetone: a) solution after 2 days at room temperature, b) initial exchange solution, c) a-b showing probable product Mo$_2$O$_3$(C$_5$HF$_6$O$_2$)$_4$
5 RESULTS AND DISCUSSION: LASER PHOTODEPOSITION OF MOLYBDENUM OXIDES

This chapter contains the results and discussion of the laser photodeposition experiments. The initial experiments were carried out in order to characterize the "standard" (perpendicular incidence) laser photodeposition process at various conditions. Subsequent experiments were performed to answer specific questions about the process such as: Which phase, gaseous or adsorbed, is the dominant source of deposited material? Is perpendicular laser incidence necessary for the formation of Mo$_{4.11}$ and if so, why (why not)? What specific oxidation and reduction reactions occur? When, where, and how do they occur? The second section contains the discussion of the results of these experiments illustrating each step of this laser photodeposition system.

5.1 Experimental Results

For all of the conditions used in this work, no deposition was ever observed without laser fluence of some
kind. During deposition with oxygen, fluorescence was noticeably quenched as compared to the fluorescence observed during the UV photodissociation of Mo(CO)$_6$ in helium only. Although attempts were specifically made to observe ozone possibly created by the UV radiation, none was ever observed by mass spectrometry. This could, however, reflect the scavenging/decomposition of ozone by the warm metal surfaces contacted before reaching the mass spectrometer. No molybdenum containing species (MoO$_2$, MoO$_3$) other than the gas phase Mo(CO)$_6$ were observed by mass spectrometry. It is unlikely that these species, if present in the gas phase, would arrive at the mass spectrometer due to their extremely low volatility. In addition, attempts were repeatedly made to detect the existence of carbonyl fragments in deposited material using Raman spectroscopy. However, Raman peaks for Mo(CO)$_6$ (extremely large 2000 cm$^{-1}$) and adsorbed or complexed CO$_x$ species (-1700-2143 cm$^{-1}$) were never observed in the deposited films. The Raman spectrum of the substrate silicon (Figure 5.1) was not subtracted out in the reported spectra and is responsible for the often observed intense peak at 521 cm$^{-1}$. Other Raman peaks of silicon are orders of magnitude less intense and are noted where relevant but in general were not observed. All thin film Raman spectra reported in this work were obtained with the exclusion of air by helium flushing and using laser powers of 100 mW or less unless otherwise noted.
Figure 5.1 Raman spectrum of Si(100) wafer
5.1.1 Characterization of the "Standard" Process

Following sections describe experiments in which some of the basic operation conditions were varied. The "standard" conditions used in this work are presented in Table 5.1 while specific variations are described below.

5.1.1.1 Effects of surface temperature

Drastically different film morphologies, appearances (color, metallic luster) and chemical content were observed over the temperature range studied. Figure 5.2 shows the smooth surface of material deposited at the standard condition 100 °C surface temperature substrate. Vaguely visible are domains or crystallites with dimensions on the order of 1000 - 2000 Å which are probably grain boundaries. This material and other deposits performed on 112 and 125 °C substrates were identical in appearance, having a deep magenta-purple color and definite metallic luster. The thickness of the deposits formed at the standard conditions was measured by ellipsometry and found to be 600-650 Å thick with a calculated index of refraction of ~2.0. The estimated thickness (limited by instrument resolution) using SEM analysis of the edge of a cleaved substrate was 500-1000 Å.

In sharp contrast, the "tree-like" fractal nature of structures deposited on a 60 °C substrate is shown in Figure 5.3a. These structures are characteristic of diffusion-limited growth processes (see Meakin [135]). This material
Table 5.1  Standard conditions for laser photodeposition experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(CO)$_6$ Concentration</td>
<td>0.10 torr (130 ppm)</td>
</tr>
<tr>
<td></td>
<td>($2.7 \times 10^{15}/\text{cm}^3$)</td>
</tr>
<tr>
<td>O$_2$ Concentration</td>
<td>20% (152 torr)</td>
</tr>
<tr>
<td></td>
<td>($4.1 \times 10^{18}/\text{cm}^3$)</td>
</tr>
<tr>
<td>Helium</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>($1.6 \times 10^{19}/\text{cm}^3$)</td>
</tr>
<tr>
<td>Total Pressure</td>
<td>1 Atm</td>
</tr>
<tr>
<td>Surface Temperature</td>
<td>100 °C</td>
</tr>
<tr>
<td>Gas Temperature</td>
<td>70-80 °C</td>
</tr>
<tr>
<td>Laser Wavelength</td>
<td>193 nm</td>
</tr>
<tr>
<td>Photon energy</td>
<td>6.42 eV 620 kJ/mol 153 kcal/mol</td>
</tr>
<tr>
<td>Laser Pulse Intensity</td>
<td>30 mJ/cm$^2$ (2.9 x 10$^{16}$ photons/cm$^2$)</td>
</tr>
<tr>
<td></td>
<td>(nominal 10 nS pulse) (3x10$^6$ W/cm$^2$)</td>
</tr>
<tr>
<td>Pulse Rate</td>
<td>8 Hz</td>
</tr>
<tr>
<td>Number of Pulses</td>
<td>4000</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si(100)</td>
</tr>
</tbody>
</table>
Figure 5.2  Morphology of $\gamma$-Mo$_4$O$_{11}$ film deposited at standard conditions: $T_{\text{surface}} = 100 \, ^\circ\text{C}$, pulse intensity = 30 mJ/cm$^2$, $[\text{Mo(CO)}_6] = 0.1 \, \text{torr}$, $[\text{O}_2] = 20\%$, 4000 pulses, perpendicular incidence
Figure 5.3a  Morphology of MoO$_2$ film deposited on 60 °C substrate with 30 mJ/cm$^2$ pulse intensity showing fractal structures resulting from diffusion limited growth

Figure 5.3b  Morphology of MoO$_2$ film deposited on 60 °C substrate with 55 mJ/cm$^2$ pulse intensity showing increased density of fractal structures
was highly absorbing black in color and had no metallic appearance. A spot deposited on the 60 °C substrate using a higher (55 mJ/cm²/pulse) than standard pulse intensity also appeared highly absorbing black. The deposited material, as shown in Figure 5.3b was comprised of structures similar in nature but significantly more dense than those observed for material deposited at the standard (30 mJ/cm²/pulse) incident intensity.

An additional difference observed at this lower temperature was the transport of particulate material to form a "tail" which trailed in the downstream direction from the laser spot as shown in Figure 5.4a. Small clusters of material which appeared to be fragments of the larger structures in the spot were observed in the downstream tail and are shown in Figure 5.4b. No such tail was observed for the high incident intensity, 60 °C deposit (also shown in Figure 5.4a) or for any case in which the surface temperature was above 80 °C.

During Raman studies of these films, it was discovered that the low temperature, (60 °C), "fractal structure" deposits could be easily (at the lowest possible powers) transformed to α-MoO₃ during exposure to the Raman laser (Ar⁺ 514 nm) if air or pure oxygen was present in the Raman cell. The higher temperature films were much more resistant to changes. Even 10 minute exposures at 300 mW in oxygen caused no observable changes in their Raman spectra.
Figure 5.4a  Downstream "tail" of deposit performed on 60 °C substrate with 30 mJ/cm² pulse intensity. Spot at top deposited on 60 °C surface with 55 mJ/cm² pulse intensity with no "tail"

Figure 5.4b  Morphology of material in downstream "tail"
Figure 5.5 shows the Raman spectrum of a film deposited on the "standard condition" 100 °C substrate. Films deposited at temperatures of 100, 112, and 125 °C gave virtually identical spectra showing intense peaks at 908 cm$^{-1}$, 835 cm$^{-1}$ with a shoulder at 845 cm$^{-1}$, and 789 cm$^{-1}$ on top of a broad hump extending from 600 cm$^{-1}$ to approximately 1000 cm$^{-1}$. A weak broad peak was evident at 730 cm$^{-1}$ and very weak peaks were observed at 880 and 980 cm$^{-1}$. Another broad hump beginning at approximately 500 cm$^{-1}$ extended to lower wavenumbers. Peaks of medium intensity were observed at 452, 430, 378 and 183 cm$^{-1}$ while weak peaks were observed at 407, 350, 306, 276, 226, and 195 cm$^{-1}$. The Raman spectra of these films exhibit a virtually identical match with the spectrum of solid $\gamma$-Mo$_4$O$_{11}$ (Figure 3.7) and do not show the distinctive 958, 335, 322, and 201 cm$^{-1}$ peaks exhibited by the alternative structure $\eta$-Mo$_4$O$_{11}$. The relatively low level of Rayleigh scattering generated by these "standard condition" films allowed the study of the low wavenumber region of the Raman spectrum.

Figure 5.6 shows the low wavenumber Raman spectrum of a "standard condition" film. The obvious peak at 86 cm$^{-1}$ and the smaller peak at 163 cm$^{-1}$ are at frequencies too low to be attributed to anything other than acoustic (lattice) vibrations. These frequencies are in the range of lattice vibrations for molybdenum oxides as seen at 82 and 158 cm$^{-1}$ for $\alpha$-MoO$_3$ and at 77 and 128 cm$^{-1}$ for $\beta$-MoO$_3$ as reported
Figure 5.5  Raman spectrum of $\gamma$-Mo$_4$O$_{11}$ film deposited at standard conditions on Si(100)
Figure 5.6  Raman spectrum of $\gamma$-Mo$_4$O$_{11}$ film deposited at standard conditions on Si(100) showing low wavenumber lattice vibrations
previously \cite{65,66}. This indicates that the film has definite long range order, i.e., crystallinity. It is also interesting to note that $\alpha$-$\text{MoO}_3$, $\beta$-$\text{MoO}_3$, and $\gamma$-$\text{Mo}_4\text{O}_{11}$ have such similar lattice vibrations at 82, 77, and 86 cm$^{-1}$ respectively.

Depositing a row of 5 identical spots under standard conditions made it possible to obtain information about the crystallinity of the deposited films using a large film Debye-Scherrer ("Read") X-ray camera. The observed d-spacings and approximate intensities are presented in Table 5.2 and identify the material as polycrystalline (no evidence of preferred orientation) $\gamma$-$\text{Mo}_4\text{O}_{11}$. Energy dispersive X-ray analysis was performed and detected only Si, Mo, and O in these films. Carbon was not observed above the estimated 2-3% detection limit. The carbon content of the standard $\text{Mo}_4\text{O}_{11}$ film was measured by AES after approximately 60% of the film thickness had been removed by sputtering. The carbon content was estimated at 2.5% (atomic) while a small amount (<1%) of nitrogen was also observed. It is likely that most of this carbon and nitrogen is a result of the adsorption of atmospheric hydrocarbons, CO$_2$, and nitrogen on the surface (in the grain boundaries) of the $\text{Mo}_4\text{O}_{11}$ crystallites. Auger profiles indicated that the "surface" nitrogen was "underneath" the "surface" carbon.

A Raman spectrum of the black rough film deposited at 60 °C is shown in Figure 5.7a. Peaks are evident at 743,
Table 5.2 X-ray Read camera data for standard Mo₄O₁₁ film.

<table>
<thead>
<tr>
<th>Deposited Film</th>
<th>(\gamma)-Mo₄O₁₁ (JCPDS-ICCD 5-0337)</th>
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<tr>
<td>Read Camera X-ray mm</td>
<td>d(Å)</td>
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<tr>
<td>----------------</td>
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<tr>
<td>21.3</td>
<td>4.15</td>
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<tr>
<td>22.5</td>
<td>3.93</td>
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<tr>
<td>22.8</td>
<td>3.88</td>
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<td>24.0</td>
<td>3.69</td>
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<tr>
<td>26.0</td>
<td>3.41</td>
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<td>32.4</td>
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<td>33.6</td>
<td>2.65</td>
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<td>34.3</td>
<td>2.60</td>
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<td>53.1</td>
<td>1.72</td>
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<td>56.9</td>
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<tr>
<td>25.1</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Note: Only the strongest lines are observed. The d-spacing discrepancy is due mainly to the uncertainty in determining the zero point on the Read camera film.
Figure 5.7  Raman spectrum of black films deposited on 60 °C substrate. a) with 30 mJ/cm$^2$ intensity, b) with 55 mJ/cm$^2$ intensity
570, 496, 424, 360, 229, and 205 cm\(^{-1}\). The spectrum of the film deposited at 60 °C and higher intensity (55 mJ/cm\(^2\) pulse) gave the same peaks, as seen in Figure 5.7b, but with significantly higher signal to noise ratio allowing the resolution of the 570 cm\(^{-1}\) peak into 570 cm\(^{-1}\) with a 587 cm\(^{-1}\) shoulder and the 360 cm\(^{-1}\) peak into 361, and 349 cm\(^{-1}\). These spectra positively indicate the presence of MoO\(_2\) by virtue of the excellent spectral match with solid MoO\(_2\) (Figure 4.5). Energy dispersive X-ray analysis of these black particulate films detected Si, Mo, O with no evidence of carbon (estimated detection limit -2-3%), as shown by Figure 5.8.

5.1.1.2 Effects of pulse intensity Depositions were performed using various incident pulse intensities while maintaining a constant total photon exposure (different total number of pulses). Again noticeable changes were easily observed in the color of the deposited material. At the lowest intensity, 10 mJ/cm\(^2\) pulse, the deposit was translucent yellow-green-grayish material. Between 10 mJ/cm\(^2\) pulse and the standard condition 30 mJ/cm\(^2\) pulse, the deposit color went through a continuous transition from yellow-green transparent to blue-green translucent to dark blue-purple opaque to purple-magenta metallic. Material deposited at a higher intensity, 42 mJ/cm\(^2\) pulse, was not visibly different from that deposited at the standard intensity.

Selected Raman spectra from the above series of deposits, as well as a parallel incident deposit, are
Figure 5.8  Energy dispersive X-ray spectrum of black film deposited at 60 °C with 30 mJ/cm²
presented in Figure 5.9a-d. At parallel incidence, (5.9a), the perpendicular incident intensity is zero and only large humps centered 850 cm\(^{-1}\) and 400 cm\(^{-1}\) are observed in the Raman spectrum. Increasing the perpendicular incident intensity to 10 mJ/cm\(^2\)pulse, (5.9b), leads to the superposition of small peaks on top of the large humps. The peaks are located at approximately 908, 880, 830, 790, and 380 cm\(^{-1}\) and indicate the presence of Mo\(_4\)O\(_{11}\). At the standard perpendicular incident intensity of 30 mJ/cm\(^2\)pulse, (5.9c), well defined \(\gamma\)-Mo\(_4\)O\(_{11}\) is observed. At a pulse intensity of 42 mJ/cm\(^2\)pulse, a large peak at 880 cm\(^{-1}\) is observed in coexistence with the Mo\(_4\)O\(_{11}\) peaks (5.9d).

Although the Raman spectrum of the solid Mo\(_8\)O\(_{23}\) was not studied (verified) in this work, Raman spectra performed previously in this group [125] show that Mo\(_8\)O\(_{23}\) has a very large peak at 879 cm\(^{-1}\) and a much smaller peak around 813 cm\(^{-1}\). The largest peak at 880 cm\(^{-1}\) was observed for material deposited at approximately 60 mJ/cm\(^2\)pulse and 4 Hz pulse rate.

5.1.1.3 Effects of oxygen concentration

Depositions were performed using various oxygen concentrations ranging from 26% to 0.28%. Raman spectroscopy showed the existence of \(\gamma\)-Mo\(_4\)O\(_{11}\) in the purple films deposited with 26% to 2.6% \(O_2\). However, with decreasing oxygen concentration, the silicon substrate peak at 521 cm\(^{-1}\) decreased in intensity. At 1.4% \(O_2\) the resulting film was
Figure 5.9  Raman spectra of films deposited by perpendicular incidence with intensities a) 0 mJ/cm$^2$(parallel), b) 10 mJ/cm$^2$, c) 30 mJ/cm$^2$, and d) 42 mJ/cm$^2$
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gray-black. Weak Raman peaks were observed at approximately 740 cm$^{-1}$ and 205 cm$^{-1}$ corresponding to the two most intense peaks of MoO$_2$. Further decrease in the oxygen concentration to 0.28% led to a brown-black film giving a relatively featureless flat Raman spectrum in which the silicon 521 cm$^{-1}$ peak was not observed. It is probable that the deposited films have increasing amounts of molybdenum metal which will efficiently reflect the incident Raman laser as well as attenuate the scattered radiation thus preventing observation of the underlying silicon substrate spectrum.

5.1.2 Parallel Laser Incidence Experiments

With the laser beam (at standard intensity) passing parallel over the 100 °C substrate surface, a "stripe" of yellow-green-gray material was deposited. This material appeared transparent from all viewing angles and looked very similar to the film deposited using the lowest intensity (10 mJ/cm$^2$/pulse) perpendicular incidence. In contrast, the film deposited with parallel incidence on a 60 °C substrate appeared gray opaque when viewed at an angle with respect to the surface normal. Morphologies of the films deposited with parallel incidence on 100 °C and 60 °C substrates are shown in Figures 5.10a and 5.10b respectively. The structures observed in the 60 °C deposit are very similar to the fractal structures observed for the 30 mJ/cm$^2$/pulse perpendicular
Figure 5.10a Morphology of film deposited by parallel beam on 60 °C substrate showing fractal structures

Figure 5.10b Morphology of film deposited by parallel beam on 100 °C substrate showing small clusters
incident deposition performed on a 60 °C substrate. Deposited on a 100 °C substrate, the film exhibits the smaller cluster morphology with "loosely packed" domains with dimensions on the order of 1000-2000 Å.

The Raman spectrum of this film (deposited on a 100 °C surface) was shown previously in Figure 5.9a and is shown in greater detail in Figures 5.11 and 5.12. In Figure 5.11 a bare silicon Raman spectrum is shown for comparison. Figure 5.12 shows the result of subtraction of most of the bare silicon leaving only the deposited film spectrum which clearly shows the smooth broad humps centered at 850 and 400 cm⁻¹. The lack of distinct peaks is indicative of "amorphous" structure (i.e., highly distorted with a lack of short range order).

An estimate of the average stoichiometry of the 100 °C parallel deposit was obtained by annealing the sample at 350 °C for 5 hours in a sealed argon-filled quartz tube. Raman spectroscopy (Figure 5.13) showed the presence of a mixture of two discrete molybdenum oxides, MoO₂ and Mo₄O₁₁, in the annealed film indicating an average stoichiometry between MoO₂ and Mo₄O₁₁. The morphology of the post-annealed film appeared the same as the as-deposited film with 1000-2000 Å domains. For both the 100 °C and the 60 °C parallel deposits, only molybdenum, oxygen, and the silicon substrate were detectable by EDS.
Figure 5.11  Raman spectrum of film deposited by parallel beam on 100 °C substrate (a), "Bare" silicon substrate shown for comparison (b)
Figure 5.12 Raman spectrum of film deposited by parallel beam on 100 °C substrate (after subtraction of most of "bare" silicon substrate spectrum) showing broad features of amorphous film
Figure 5.13  Raman spectrum of film deposited by parallel beam on 100 °C substrate after 5 hr, 350 °C anneal in argon showing intermediate stoichiometry (mixture of $\text{Mo}_4\text{O}_{11}$ and $\text{MoO}_2$)
5.1.3 Sequential parallel/perpendicular incidence.

Changes were induced in the yellow-green-gray "transparent" parallel deposited stripe by exposing the material to perpendicularly incident laser radiation. Directly after 100 °C parallel deposition, the cell was flushed with helium to remove all gaseous reactive species. Different materials were produced by varying the intensity and number of perpendicularly incident laser pulses.

Raman spectra from these materials are shown in Figure 5.14a-d. After exposing the parallel deposited film (5.14a) to only one pulse at ~10 mJ/cm² pulse, an unmistakable color change occurs resulting in a purple spot. A magenta-purple spot was created by approximately 40 pulses at the standard intensity (30 mJ/cm² pulse). The Raman spectrum of this deposit is shown in spectrum (5.14b). Peaks at 908, 835, 795, 730, and 430 cm⁻¹ indicate the presence of Mo₄O₁₁ species. The origin of the peak at 940 cm⁻¹ has not been determined. A tan-gray metallic spot was formed from the parallel deposited material by increasing the exposure and intensity to approximately 400 pulses at 60 mJ/cm² pulse. The Raman spectrum of this spot (5.14c) shows weak peaks at 743, 364, 349, 229, and 205 cm⁻¹ clearly signaling the presence of MoO₂. The Raman spectrum of the silicon substrate is shown (5.14d) for comparison.
Figure 5.14 Raman spectrum of film deposited by parallel beam on 100 °C substrate (a), after exposure to perpendicular incident pulses: b) ~40 at 30 mJ/cm², c) ~400 at 60 mJ/cm², d) "bare" Si(100)
5.1.4 Lattice Influence: Si(111) experiment

Since one of the lattice constants of $\gamma$-Mo$_4$O$_{11}$ (5.457 Å) matches nearly exactly with Si(100) (5.431 Å), there was a possibility of epitaxial influence on the film growth by the Si(100) (or very thin structure retaining SiO$_2$ layer) surface. A silicon substrate, Si(111), with no lattice constants which matched $\gamma$-Mo$_4$O$_{11}$ was used for a deposition experiment. The resulting deposited film was identical in appearance and gave a Raman spectrum identical to films deposited on Si(100). This indicated that the Si(100) lattice had no influence in determining the $\gamma$-Mo$_4$O$_{11}$ stoichiometry or structure.

5.1.5 Other Observations

Some depositions were performed using more than 4000 pulses at otherwise standard conditions. It was observed that the growth process apparently changes at 6000-7000 pulses at which time the deposit surface begins to appear yellow-green-gray in color similar to the parallel deposited films. This phenomenon was not investigated further.
5.2 Discussion of Results

This discussion is organized in sections which each describe a particular step in the chronological sequence of events during the laser photodeposition of thin film Mo₄O₁₁ from gas phase Mo(CO)₆ and oxygen. Experimental results are discussed and compared with relevant literature. Also included is a section which addresses possible explanations for the lack of carbon contamination in the deposited films. Many techniques have been used to produce molybdenum oxide films although crystalline films with stoichiometries between MoO₂ and MoO₃ have never been reported before this work. In light of this a section is included which presents the unique aspects of the laser photodeposition process which are essential for the production of crystalline Mo₄O₁₁.

5.2.1 Gas Phase Source/Photolytic Activation

5.2.1.1 Experimental evidence A variety of experimental results reveal that the gaseous Mo(CO)₆ acts as the primary source of molybdenum atoms. Parallel beam experiments performed in this work show that molybdenum oxide material is deposited with no photons impinging on the surface. Solanki et al. [136] have also observed deposition (in the absence of oxygen) of molybdenum with parallel incidence although the films were highly contaminated with
carbon and oxygen. The fractal "tree-like" structures observed for low surface temperature depositions clearly indicate a diffusion limited gas phase process. Blue-green fluorescence was observed in the absence of oxygen indicating that the dissociation of the Mo(CO)$_6$ is photolytic in nature. Fluorescence has been observed previously by Solanki et al. [136], Gilgen et al. [20], and Flynn et al. [30] during attempts to deposit metallic molybdenum from Mo(CO)$_6$.

5.2.1.2 Absorption cross section and photolytic control

A 193 nm photon (6.42 eV, 148 kcal/mol) has enough energy to break up to four Mo-CO bonds in Mo(CO)$_6$ ($D_{\text{mean}} = 36$ kcal/mole, $D_1 = 40$ kcal/mol [23,26,27]). This process is presented in Equation 5.1. Complete removal of CO ligands has been observed only for systems with photon fluences large enough to cause multiphoton dissociation (MPD) [36]. In 760 torr of pure helium, the excited complex can undergo MPD to produce Mo$^*$ which relaxes by emitting blue-green fluorescence. Photolysis products in low temperature matrices with $x = 5, 4, \text{ and } 3$ have been previously observed for photolysis at wavelengths greater than 285 nm [31]. As presented below, the process leading to the deposition of one Mo atom is

$$\text{Mo(CO)}_6 + h\nu (193\text{ nm}) \rightarrow \text{^*Mo(CO)}_x + (6-x)\text{CO} \quad x \leq 4 \quad (\text{Eq. 5.1})$$
likely the result of the absorption of one photon as opposed to a multiphoton process.

Iverson and Russel [29] have reported $\sigma_{193}$ to be $1.8 \times 10^{-18}$ cm$^2$. Flynn and co-workers [30] have reported a $\sigma_{193}$ of $6 \times 10^{-17}$ cm$^2$ using a nonstandard definition of $\sigma_{193}$. Conversion of this to the standard definition of $\sigma_{193}$ gives a value of $1 \times 10^{-18}$ cm$^2$ in good agreement with that in reference [29]. By assuming an efficiency of unity for the photoreactions which occur in this work and assuming that all Mo(CO)$_6$ molecules which absorb a photon contribute to the observed deposited film, a cross section can be calculated using Beer's law. Concentrations of Mo(CO)$_6$, O$_2$, and He as well as the photon flux for "standard" conditions which produced 650 Å thick films of γ-MoO$_4$ were presented previously in Table 5.1. The result of the calculation of $\sigma_{193}$ (see Appendix A) for this work was $1.8 \times 10^{-18} \pm 0.8 \times 10^{-18}$ cm$^2$ which is in excellent agreement with that reported by other investigators. This one-to-one correspondence of deposited Mo atoms with photons absorbed by gaseous Mo(CO)$_6$ indicates that a one-photon process is responsible for the generation of the molybdenum contained in the observed deposits.

5.2.1.3 Thermal decomposition on laser-heated surface Since Mo(CO)$_6$ undergoes thermal decomposition at ~125-140 °C, collisions with a hot surface could lead to deposition of material. A model was used to estimate (see
Appendix B) the surface temperature rise of a silicon substrate induced by various laser pulse intensities. The absorption length of silicon for 193 nm photons is $6 \times 10^{-7}\text{cm}$ [137]. This is very small compared to the characteristic thermal conduction length in silicon, $(2\kappa\tau)^{1/2} = 1 \times 10^{-4}\text{ cm}$, where $\kappa$ is the thermal diffusivity of silicon and $\tau$ is the laser pulse length. This allows the mathematical model to be simplified to the case of a constant flux at the surface which leads to a simple analytic function for the surface temperature rise [138,139].

Figure 5.15 shows the estimated rise in surface temperature for the range of intensities used in this work. For a 30 mJ/cm$^2$ pulse (3 MW/cm$^2$ for a 10 ns pulse) impinging on a 100 °C surface, the temperature rise is estimated to be 100 °C (evaluating the nearly constant physical properties at 150 °C). This results in a peak surface temperature of 200 °C which would be enough to decompose Mo(CO)$_6$. However, since the heating is controlled by the conduction rate into the silicon, the cooling of the surface after the laser pulse will be controlled by the same mechanism. Consequently the surface temperature will drop over approximately the same time scale as the rise.

A conservative estimate of the length of time necessary for the surface temperature to relax to its pre-pulse value is 100 ns. Using this time it is possible to calculate the number of Mo(CO)$_6$ molecules which impact the surface during
Figure 5.15  Estimated silicon surface temperature rise induced by ~10 ns pulse of 193 nm laser radiation of varying intensity with silicon thermal properties evaluated at various intermediate temperatures
the short "hot" period. A surface collision rate of $1 \times 10^{19}$/cm$^2$/s (see Appendix C) leads to $1 \times 10^{12}$ molybdenum atoms/cm$^2$/pulse which is 30 times smaller than the observed deposition rate of $3 \times 10^{13}$ Mo atoms/cm$^2$/pulse. Therefore it is unlikely that the decomposition of Mo(CO)$_6$ molecules on the laser heated surface contributes significantly to the observed deposition process. As the film grows, the optical and thermal properties of the depositing film surely contribute to the effective surface temperature. The relative reflectivity of the bc plane from 200-900 nm has been reported [81] although no indication of the absolute reflectivity is given. Currently no thermal conductivity measurements are available for the anisotropic Mo$_4$O$_{11}$ compounds.

5.2.2 Possible Subsequent Gas Phase Reactions

It is assumed that the gas phase reactions which may occur would be unaffected by small changes in gas temperature. Introduced to the cell at approximately 75 °C, the reactant gas could warm slightly over the 100 °C surface or cool slightly over the 60 °C surface, but these changes are assumed to be insignificant in the analysis of the gas phase reactions which have been shown to be photolytically initiated.
Based on the results of this work, it is impossible to determine which, if any, gas phase reactions occur subsequent to the initial photodissociation of Mo(CO)$_6$. Attempts were made to detect CO$_2$ by mass spectrometry during depositions, but the production of CO$_2$ was never observed. The relative lack of carbon in the films indicates that any remaining CO ligands are lost either in a gas phase reaction or by desorption from the deposit surface. This section presents some possibilities for gas phase reactions leading to "intermediate" species.

**5.2.2.1 Possible creation of gas phase MoO$_2$ species**

With 20\% O$_2$ present during photodeposition, fluorescence is not observed. The fluorescence is quenched by collisions and possible reaction with an O$_2$ molecule. Collisions with O$_2$ occur once every $4 \times 10^{-10}$ s which is fast relative to the ~10 ns laser pulse length and ns-μs fluorescence timescale. After photodissociation the resulting coordinatively unsaturated zero-valent sub-carbonyl species would be expected to be very reactive. Fletcher and Rosenfeld have shown that the photolytically produced gas phase Cr(CO)$_4$ fragment reacts at nearly the hard sphere collision rate with a variety of species [33-35]. Based on their proposed relationship of rate constants with ligand ionization potentials, oxygen would also be expected to react with the sub-carbonyl fragment at near hard sphere collision
One obvious process to consider is reaction with oxygen as shown in Equation 5.2. Gaseous \( \text{MoO}_2(\text{CO})_z \) species

\[
\text{Mo(CO)}_x + \text{O}_2 \leftrightarrow \text{MoO}_2(\text{CO})_z + (x-z)\text{CO}
\]  
(Eq. 5.2)

have never been reported before, but surface species with \( z = 2 \) have been reported by Burwell and Brenner in studies of catalysts prepared by supporting \( \text{Mo(CO)}_6 \) on \( \gamma-\text{Al}_2\text{O}_3 \) [140]. In addition, the authors report the removal of three CO ligands from supported \( \text{Mo(CO)}_6 \) leaving an adsorbed \( \text{Mo(CO)}_3 \) species.

Formation of \( \text{MoO}_2(s) \) is an exothermic reaction with \( \Delta H_f = -140 \text{ kcal/mol} \) [86]. With an estimated \( \Delta H_{\text{vap}} \) of 125 kcal/mole [141], the \( \Delta H_f \) of \( \text{MoO}_2(g) \) is -15 kcal/mole. The heats of formation for \( \text{Mo(CO)}_6(g) \) and \( \text{CO}(g) \) are -219 kcal/mole and -26.4 kcal/mol respectively [28]. A net reaction for the photolytically initiated production of \( \text{MoO}_2(g) \) from \( \text{Mo(CO)}_6(g) \) and \( \text{O}_2(g) \) is shown in Equation 5.3.

\[
\text{Mo(CO)}_6(g) + \text{O}_2(g) + \text{hv} \leftrightarrow \text{MoO}_2(g) + 6\text{(CO)}
\]  
(Eq. 5.3)

193 nm \( \text{hv} = 153 \text{ kcal/mole} \) \( \Delta H_{\text{rxn}} = -77 \text{ kcal/mole} \)

This resulting reaction is exothermic and consequently would be thermodynamically favorable. On condensing on the surface, the heat of vaporization would be liberated
providing an additional driving force for CO loss of -125 kcal/mol.

5.2.2.2 Gas phase oxidation \( \text{O}_3 \) vs. \( \text{O}_2 \) Ozone, a strong oxidant, is known to form from molecular oxygen in the presence of UV radiation and should be considered a possible reactant in photodeposition systems in which oxidation processes occur. Analysis of data presented by Noyes et al. \cite{142} and Granath \cite{143} results in cross sections (at 193 nm), \( \sigma_{193} \), for the production of ozone from 20% oxygen in helium of \( 4 \times 10^{-21} \text{cm}^2 \) and \( 8 \times 10^{-22} \text{cm}^2 \) respectively. Using Beer's law and the larger \( \sigma_{193} \) it can be estimated (Appendix B) that \( 9 \times 10^{13} \) molecules/cm\(^2\) pulse of \( \text{O}_3 \) (\( 4 \times 10^{14}/\text{cm}^3 \)) are created in the estimated 2 mm thick reactant gas layer used in this work.

Assuming that the collision cross section for \( \text{Mo(CO)}_x-\text{O}_3 \) collisions is approximately the same as for \( \text{Mo(CO)}_6-\text{Mo(CO)}_6 \) allows the calculation of the \( \text{O}_3 \) collision rate for a single gaseous \( \text{Mo(CO)}_x \) species. The calculated rate (see Appendix C) of \( 3.1 \times 10^5/\text{s} \) is less than the \( \text{Mo(CO)}_x-\text{Mo(CO)}_6 \) rate of \( 8.1 \times 10^5/\text{s} \) and 4 orders of magnitude lower than the \( \text{Mo(CO)}_x-\text{O}_2 \) rate of \( 2.3 \times 10^9/\text{s} \). An alternative comparison can be made by expressing the thickness of the reactant layer (maximum distance to the substrate) as the number of mean free paths (MFP's) between collisions of a particular gas phase species with the activated molybdenum species. The reactant layer is 9100 \( \text{O}_2 \) MFP's thick indicating that the
activated molybdenum species will undergo a large number of oxygen collisions before reaching the surface. On the other hand it is much less likely that the activated molybdenum species will form a carbonyl cluster by colliding with Mo(CO)$_6$ or react with O$_3$ because the reactant layer thicknesses for these species are only 10 and 1.5 MFP’s respectively.

With no available data on the relative reactivities of O$_3$ and O$_2$ with Mo(CO)$_x$ species, it is impossible to determine whether O$_3$ is important. However, it has been shown that the coordinatively unsaturated zero-valent Cr(CO)$_4$ sub-carbonyl fragment produced from Cr(CO)$_6$ at 248 nm is extremely reactive with reaction rate constants nearly equal to the hard sphere collision rates [33-35]. It seems likely that the primary photoproduct Mo(CO)$_x$ species would also be extremely reactive and consequently react with the first available oxidizing molecule. In this case reaction with O$_2$ would be expected to dominate due to its much higher collision rate.

Many attempts were made but O$_3$ was never observed with the mass spectrometer during photodeposition. If O$_3$ was participating in the oxidation processes, species other than MoO$_2$ would be expected. However, at the low, 60 °C, surface temperature, MoO$_2$ was observed exclusively. Even at 55 mJ/cm$^2$ pulse, which would produce approximately twice the ozone of the standard intensity, only MoO$_2$ was observed. In
addition, participation by ozone is unlikely in this case because it is at very low concentrations. Mo(CO)\textsubscript{x} - O\textsubscript{3} collisions would occur on a time scale which is similar to that for fluorescence processes (10\textsuperscript{-6} s) and fluorescence would probably still be observed.

5.2.3 Diffusion of intermediate species to surface

For the purpose of discussion, the molybdenum species resulting from gas phase reactions will be referred to as "the intermediate" or as *MoO\textsubscript{y}(CO)\textsubscript{z} with the understanding that y and/or z could be zero. The transport of the intermediate is diffusion limited. The fractal structures observed in the 60 °C depositions are characteristic of diffusion limited deposition processes with low reactant concentrations, high sticking coefficients, and low surface mobilities (see Meakin [135]).

The intermediate species in the gas phase would be expected to have low vapor pressure and consequently condense readily on the deposit surface. A higher sticking coefficient would be expected on a lower temperature surface. Thus the downstream "tail" observed at 60 °C is probably not the result of gas phase agglomeration of particulates. Instead it is believed that the tail is comprised of particles resulting from the fracturing of the fractal structures. These fragments are subsequently convected
downstream. The similarity of the structures observed in both the tail and deposit (Figures 5.5 and 5.4) supports this view. The lack of a tail for the higher intensity low temperature deposition is consistent with the more dense structures produced as a result of increased surface mobility (higher surface temperature) during the more intense laser pulse.

One obvious requirement for the formation of gas phase particulates is that gas phase collisions compete effectively with condensation on the deposit surface. The mean free path of $^\text{MoO}_y(CO)_z$-$\text{Mo(CO)}_6$ collisions is estimated to be ~0.02 cm. As stated earlier, this is only 10 times smaller than the maximum distance (reactant gas layer thickness) to the surface and indicates that cluster formation is not very likely in relation to deposition.

It is also possible that a significant concentration gradient develops during the diffusion of the intermediate to the surface. The mean free path of the intermediate species in He of 68 nm is very short relative to the 2 mm thick gas layer. In addition, using a characteristic time, t, determined by the gas velocity (~4 cm/s) and the deposit diameter (1 mm), the characteristic diffusion length $(Dt)^{1/2}$ $(D = \text{Gas phase diffusivity estimated } 0.2 \text{ cm}^2/\text{s})$ is 0.07 cm. This is similar to the reactant gas layer thickness and implies that the surface could be acting as a "sink" in this diffusion limited transport.
5.2.4 Oxidation of Surface Species

5.2.4.1 Oxidation by O₂

Only MoO₂ was observed for depositions performed on 60 °C surfaces. By increasing the surface temperature to 100 °C, the more oxidized MoOₓ (2 ≤ x ≤ 2.75) material was produced in both parallel and perpendicular incident depositions. It is apparent that the intermediate, MoO₀ₓ(CO)₂, arrives at the surface of the deposit with y ≤ 2. Any oxidation (if y < 2) is limited to y = 2 on a 60 °C surface. At this stage, the surface species will be considered to be MoO₂ since no evidence of substantial amounts of C or CO was ever observed in the films. At this time, it is not known exactly at what point the CO ligands are lost. The MoO₂ is oxidized further on a 100 °C surface resulting in a stoichiometry closer to Mo₄O₁₁. This conclusion is also supported by the observation that the low temperature deposited MoO₂ material was easily oxidized by the Raman laser radiation (514 nm) in the presence of pure oxygen or air.

5.2.4.2 Oxidation by ozone

At this time it is impossible to rule out the importance of ozone in the further oxidation which occurs on the surface of the deposit. However, the facile oxidation of reduced molybdenum oxide species at room temperature has been reported by Fleisch and Mains [144]. In that work, solid MoO₃ was exposed to 257 nm UV radiation in vacuo to create reduced molybdenum species
which were shown to oxidize easily when exposed to air. Again, it seems likely that oxidation by O₂ would dominate simply because of the preponderance of O₂ available.

5.2.4.3 Surface oxidation: between pulses vs. during pulse The stoichiometry (2 < x < 2.75) of the MoOₓ film deposited with parallel incidence on a 100 °C substrate shows that oxidation proceeds past MoO₂ on the 100 °C surface. In this case, the laser obviously cannot cause thermal oxidation by laser heating. This hypothesis is also supported by the fact that material deposited on a 60 °C surface does not oxidize past MoO₂ even when a high (55 mJ/cm² pulse) laser intensity which generates a higher peak temperature is used.

5.2.4.4 Oxidation to Mo₄O₁₁ It is possible that the oxidation of MoO₂ species at the relatively low temperature of 100 °C is somehow constrained from continuing beyond Mo₄O₁₁. The existence and high stability (with respect to both phase changes [71] and oxidation [67]) of the Mo₄O₁₁ structures imply that there is some sort of intrinsic stability associated with the assembly of three MoO₃ units and one MoO₂ unit. Blackburn and co-workers [141] have reported that the vapor pressure of (MoO₃)₃ over MoOₓ drops by a factor of 2 when 2.740 < x < 2.753.

McCarron [65] has reported that the corner shared octahedra of β-MoO₃ are metastable and collapse to the edge shared octahedra of α-MoO₃ at 250-400 °C. However, the
presence of the tetrahedral MoO$_2$ layer in the Mo$_4$O$_{11}$ compounds stabilizes the three layer slab of corner shared octahedra in Mo$_4$O$_{11}$ thereby allowing the structures to exist at temperatures up to 630 °C in the η form and up to 800 °C in the γ form [71].

Another explanation of the resulting MoO$_{2.75}$ stoichiometry is that the oxidation occurs on a time scale similar to the laser pulse rate in this work. It might be possible to produce more oxidized structures by allowing more time (slower pulse rates) for oxidation before inducing mobility with the next laser pulse.

It is also interesting (as discussed in the next section) that the species which is likely to have the highest mobility in this system is (MoO$_3$)$_3$. It is conceivable that this mobile trimer could influence the stoichiometry leading to "molecular" Mo$_4$O$_{11}$ by combination with a single MoO$_2$ species. The concept of "molecular" Mo$_4$O$_{11}$ species is also supported by the homogeneity of the stoichiometry in the deposited Mo$_4$O$_{11}$ films. It seems reasonable to expect to form a mixture of MoO$_2$ and MoO$_3$ particles in the films. Both α- and β-MoO$_3$ are excellent Raman scatterers with scattering efficiencies that are orders of magnitude (~5 for α-MoO$_3$) greater than Mo$_4$O$_{11}$ compounds and would be easily detected. This "mechanical mixture" was never observed, indicating that there is some intrinsic integrity of the Mo$_4$O$_{11}$ "ensemble" relative to MoO$_2$ and MoO$_3$.
5.2.5 Surface Diffusion Processes at 100 °C

5.2.5.1 Mobile species: experimental Small dense clusters observed in the material deposited with a parallel beam on a 100 °C surface (Figure 5.11b) could have formed as a result of the higher mobility of a) the initial MoO$_2$ species or b) the newly created MoO$_3$ species. The MoO$_2$ films deposited on a 60 °C substrate with a twice the normal intensity ($T_{\text{peak}}$ based on Si substrate ~200 °C) show evidence of increased mobility but still retain the obvious fractal structures associated with very low mobility deposition processes. For the standard perpendicular incidence deposition of γ-Mo$_{4}O_{11}$, the estimated peak temperature of the surface is 200 °C (based on silicon thermal properties). This peak temperature is similar to that for the 60 °C 55 mJ/cm$^2$ pulse deposition of MoO$_2$ but the morphologies of the two cases are strikingly different. This is one indication that MoO$_2$ is probably not the species responsible for the smooth structure of the standard condition Mo$_{4}O_{11}$ films.

5.2.5.2 Volatility of MoO$_2$ and MoO$_3$ The mobility of MoO$_2$ species is expected to be much lower than that of MoO$_3$ species due to the large difference in heats of vaporization (and corresponding surface binding energies). The heat of vaporization, $\Delta H_{\text{vap}}$, of MoO$_2$ is 130 kcal/mole whereas $\Delta H_{\text{vap}}$ for (MoO$_3$)$_3$, the predominant vapor species over MoO$_3$, is 80 kcal/mole [141,145,146]. In addition, the vapor pressure of
pressure of \((\text{MoO}_3)_3\) is 0.1 torr at 930 °K (657 °C) while \(\text{MoO}_2\)
must be heated to ~1840 °K to achieve the same vapor pressure. It seems likely that these relatively volatile
(mobile) \((\text{MoO}_3)_3\) trimers play a role in determining the morphology of the films deposited at 100 °C.

In theory, a comparison of the relative rates of diffusion of proposed mobile species and of oxidation of the
\(\text{MoO}_2\) species could aid in determining the importance of each process. Estimates of surface diffusion rates can be made
using \(\Delta H_{\text{vap}}\) data while the oxidation rates could be estimated from rate constants for the oxidation of \(\text{MoO}_2\).
Unfortunately, relevant published data on the oxidation process is limited to a publication by Iizuka et al. [124] in
which molybdenum oxide is reduced to some unknown extent in \(\text{CO}\) and reoxidized in \(\text{O}_2\). The data (Figure 9 of reference
[124]) indicate an activation energy of 46 kcal/mol.

5.2.6 Photoreduction by laser pulse

5.2.6.1 Molybdenum oxide photoreduction
Photoreduction of both \(\text{MoO}_3\) and supported molybdenum oxide catalysts has been reported. Fleisch and Mains [144] report
the \textit{in vacuo} UV (253.7 nm) photoreduction of crystalline \(\text{MoO}_3\) and subsequent reoxidation on exposure to air. The reoxidation on exposure to air did not occur when UV reduction was performed in a hydrogen atmosphere.
Photoreduction has also been observed by Deb during the study of electrochromic amorphous MoO\textsubscript{3} films [53].

Molybdenum oxide catalysts supported on SiO\textsubscript{2} have been shown to undergo photoreduction in the presence of a reducing atmosphere. Seyidmonir and Howe [147] report that supported Mo\textsuperscript{+6} can be reduced with 306 nm light to Mo\textsuperscript{+5} in a hydrogen atmosphere at 77 °K. Shelimov et al. [148] also report the formation of Mo\textsuperscript{+5} by photoreduction (320 < \lambda < 350) in H\textsubscript{2}.

In addition, they report that photoreduction in CO leads to the production of gaseous CO\textsubscript{2} and results in the formation of tetrahedral Mo\textsuperscript{+4} sites on which CO is adsorbed. This adsorbed CO desorbs at 100 °C leaving surface molybdenum oxide species. These species have very strong reducing properties and can reduce CO\textsubscript{2} and H\textsubscript{2}O at 90 °C and 150 °C respectively. The authors contend that these "superficial" sites, formed at low temperatures, are essentially "frozen" on the surface thereby preventing thermal rearrangements.

5.2.6.2 Observed laser induced reduction It is possible for the 193 nm UV photons to cause the reduction of MoO\textsubscript{x} when x > 2. This phenomenon was observed in this work in the formation of MoO\textsubscript{2} from the "amorphous" parallel deposited MoO\textsubscript{x} (2 < x < 2.75) film on exposure to approximately 400 laser pulses at 60 mJ/cm\textsuperscript{2} in a helium atmosphere (see Figure 5.14b).

Similar conditions exist during the photoreduction of supported molybdenum oxides and the photodeposition of
Mo₄O₁₁. In both cases, photons impinge on low temperature (T < 100 °C) surface molybdenum oxide species in the presence of CO. It seems likely that the reported "superficial" Mo⁺⁴ species could exist at some point during the laser photodeposition process. However, if the highly reducing sites are created it seems likely that they would immediately react with the abundant oxygen in the system. Based on the results of experiments performed in this work, it is impossible to determine if significant photoreduction occurs and/or if the tetrahedral Mo⁺⁴ species exist during the laser photodeposition of Mo₄O₁₁.

5.2.7 Laser Induced Mobility/Relaxation

5.2.7.1 Laser induced mobility/relaxation Laser pulses impinging on the substrate obviously influence the resulting morphology of the deposited films. Films deposited at 100 °C and perpendicular incidence are smooth and highly ordered (see Figure 5.2 ) whereas parallel incidence leads to material which is rough and lacks detectable long range order (see Figures 5.10a-b). The lack of long range order (as suggested by the broad features of the Raman spectrum) and rough morphology of the parallel deposited films indicate that the material deposited by a given laser pulse remains "amorphous" until the next perpendicular pulse imparts energy to the surface.
This energy leads to one or both of two processes. The first possibility is that the pulse causes an increase in mobility of surface species thereby allowing the growth of \( \gamma \)-Mo\(_4\)O\(_{11}\) crystallites. The second is that the pulse induces the relaxation of the amorphous or microcrystalline Mo\(_4\)O\(_{11}\) reducing the distortion of the "as-deposited" material. In this work, the formation of crystalline Mo\(_4\)O\(_{11}\) from the "amorphous" parallel deposited material by the perpendicular incidence of small numbers of laser pulses provides evidence for the relaxation process. It also seems likely that this process would lead to a more randomly oriented structure. This could be one of the reasons why the alternating slab orientation \( \gamma \)-Mo\(_4\)O\(_{11}\) is formed instead of the more ordered \( \eta \) phase.

Other published methods of producing molybdenum oxide films at 100 °C have led to amorphous or "microcrystalline" films lacking any long range order. Garcia and McCarron [66] maintain that increased surface mobility results in the production of the more thermodynamically stable structure for amorphous, \( \beta \)-, and \( \alpha \)-MoO\(_3\) thin films. Saito et al. [88] have reported the existence of short range structure ("microcrystallites") in MoO\(_3\) films vacuum deposited on room temperature substrates. Annealing at 350 °C in air resulted in increased "crystallinity" as evidenced by sharper diffraction patterns but they noted that the "microcrystallite" size observed by high resolution electron
microscopy did not change. Thus they concluded that the microcrystallites did not grow. Instead the authors concluded that the structure "relaxed" reducing the distortion in the microcrystallites.

In the photodepositions performed in this work, the observed change in film growth at about 6000-7000 pulses could be due to the change in thermal and optical properties of the surface as the deposit becomes thicker. One explanation of this phenomenon is that the laser induced peak surface temperature falls below some threshold necessary for the formation of the crystalline MoO$_3$.

5.2.7.2 Why not "collapsed" layer structure?

At the standard intensities used, the laser induced peak temperature is ~200 °C (based on the thermal properties of the silicon substrate). This temperature is well within the range where the corner shared octahedral slabs of β-MoO$_3$ are stable. There is therefore no reason to believe that the corner shared slabs of the MoO$_3$ deposits should "collapse" to the α-MoO$_3$ type structure.

5.2.8 Lack of Substantial Carbon Contamination

Carbon monoxide is known to dissociate on metallic molybdenum surfaces [42,43]. In light of this, it is not hard to understand why attempts to photodeposit metallic molybdenum films from Mo(CO)$_6$ result in films with high C and
O contamination. There are two possible explanations for the relative lack of carbon contamination in the laser deposited Mo$_4$O$_{11}$ films produced in this work. The first is that CO ligands are completely stripped from the intermediate molybdenum species by gas phase reaction. Thus the atomic (unlikely) or oxidized molybdenum species would arrive at the deposit surface already devoid of CO.

The second possibility is that, under the conditions studied, CO does not remain on the surface (i.e., desorbs and/or is displaced by the abundant oxygen). Muira et al. [149] report that, on MoO$_x$ ($0 < x < 3$), the amount of CO adsorption decreases drastically for the range $x \geq 2$. This indicates that CO is much less likely to adsorb on the oxidized molybdenum present in the laser deposited films.

In addition, as discussed previously, CO desorbs from photoreduced tetrahedral Mo$^{4+}$ sites at 100 °C [148]. Bowman and Burwell [150] report that CO adsorbed on alumina supported catalysts prepared from Mo(CO)$_6$ is completely displaced (without reaction) by O$_2$ at room temperature. Ko and Madix [91] have reported that oxygen on molybdenum surfaces inhibits the adsorption of CO. Finally, Iizuka et al. [124] have shown that MoO$_3$ is inactive for CO oxidation below 350 °C.
5.2.9 Unique Aspects of Laser Photodeposition of Mo$_4$O$_{11}$

Thin films of molybdenum oxides have been produced by a variety of techniques, but crystalline Mo$_4$O$_{11}$ has never been reported before. The laser deposition process studied in this work involves unique processes which are believed to be instrumental in the production of Mo$_4$O$_{11}$.

5.2.9.1 "Cold" (low mobility) surface MoO$_2$. It is believed that the existence of low mobility (low temperature surface) MoO$_2$ species is necessary for this process. Most evaporation and sputtering techniques start with MoO$_3$ targets. In other cases, metallic Mo targets are used but oxygen concentrations are such that target oxidation results in the sputtering of MoO$_3$. In plasma enhanced CVD of amorphous MoO$_3$ from Mo(CO)$_6$ in O$_2$ plasma, the gas phase reaction is initiated by O atoms in the plasma. This clearly is not the same as the photolytic "stripping" of CO ligands in O$_2$ and is likely to lead to species other than MoO$_2$.

5.2.9.2 Fast pulse induced crystallinity. In the laser deposition process, the stoichiometry (oxidation) develops at 100 °C. The resulting material is "crystallized" by the 10 ns laser pulse without significantly influencing the low temperature thermal oxidation. Other processes might be able to achieve the correct stoichiometry but could not achieve the crystallinity at 100 °C. The resulting amorphous
films could possibly be annealed at high temperatures in an inert atmosphere to induce crystallinity. This technique however might be more likely to produce films with significantly different surface morphologies than those produced by the "layer by layer" pulsed laser deposition.
6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1) Small area (defined by laser beam) polycrystalline thin films of Mo$_4$O$_{11}$ (predominantly γ-phase) can be deposited by UV laser photodeposition from Mo(CO)$_6$ in an oxygen containing atmosphere. Noncrystalline material deposited by parallel beam deposition at 100 °C can be "developed" by the formation of crystalline magenta/purple Mo$_4$O$_{11}$ on exposure to perpendicularly incident laser pulses.

2) The reaction(s) leading to the deposition is (are) initiated in the gas phase by the photodissociation of Mo(CO)$_6$. The absorption of one photon leads to the deposition of one Mo atom.

3) CO ligands are completely removed at some point after the initial photolysis of Mo(CO)$_6$ and before the existence of MoO$_2$ on the surface.

4) Oxidation past MoO$_2$ proceeds by thermal mechanisms on the 100 °C surface and occurs without laser induced surface heating.
5) The laser imparts energy to the surface species deposited by previous pulses. This energy performs one or both of two functions. The first is to increase the mobility and enhance the diffusion of surface species thereby allowing the growth of crystallites. The second function is to induce relaxation of "amorphous" or microcrystalline Mo$_4$O$_{11}$ domains.

6) Two unique factors in the studied pulsed laser deposition system lead to the formation of polycrystalline Mo$_4$O$_{11}$. The first is the existence of MoO$_2$ on a surface which is not hot enough to induce complete oxidation to MoO$_3$. The second factor is the laser pulse which imparts enough energy to the surface to induce crystalline structures but is too short to induce additional oxidation of Mo$_4$O$_{11}$.

7) The surface Raman cell designed for this work, when used in conjunction with the modified photodiode array detector, allows the easy collection of high quality Raman spectra of extremely thin films (<600 Å) of material with poor Raman scattering characteristics.

8) MoO$_3$ containing material can be "written" with an argon ion laser by the decomposition of spun on Mo$_2$(CF$_3$CO$_2$)$_4$ films.
6.2 Recommendations

1) Determine whether additional molybdenum oxide phases can be produced by combining longer oxidation times between pulses (both perpendicular and parallel) with surface temperatures above 100 °C and/or higher oxygen concentrations (100% O₂). Determine whether stoichiometry is "pinned" to Mo₄O₁₁ at 100 °C and 8 Hz.

2) Add H₂O vapor to reactant gas to attempt to make molybdenum-hydrogen bronze type materials. (NOTE: adding H₂ with O₂ could be very dangerous).

3) Co-feed W(CO)₆ to attempt to make MoₓWyOz intercalation structures.

4) Deposit material in UHV chamber on SiO₂ covered Si substrate to mimic process which supposedly occur on silica supported molybdenum oxide catalysts. Try to observe high activity "superficial" tetrahedral sites by subsequently adsorbing CO, O₂, N₂, CO₂ and performing temperature programmed desorption (TPD) or laser induced desorption. Anneal/reduce/oxidize deposited material and perform TPD.

5) Raman surface cell can easily see 170 "monolayers" of the poor scatterer Mo₄O₁₁. Determine collection limits of Raman surface cell for monolayers of adsorbed species (CO adsorption on Pt or Pd film on Si (use Si for alignment of optics)).
6) Perform laser photodeposition in conjunction with in situ spectroscopic techniques such as surface Raman or Infrared Reflection-Absorption (IRRAS) to observe surface MoO$_2$ or MoO$_y$(CO)$_z$ species. (Note: IRRAS must have a highly reflecting substrate.)

7) Use in situ surface Raman and/or IRRAS to look for evidence of surface (MoO$_3$)$_3$ trimers at reaction temperatures.

8) Perform photodissociation of Mo(CO)$_6$ in gas phase O$_2$ in FTIR absorbance mode to look for identity of possible gas phase intermediates such as MoO$_2$ or MoO$_y$(CO)$_z$ or collaborate with the group working on Cr(CO)$_6$.

9) Perform depositions with reactant atmospheres containing nitrogen to: a) understand why nitrogen was apparently adsorbed or reacted at the crystallite grain boundaries of air exposed samples and b) determine whether the sub-carbonyl species is active enough to react with N$_2$ thus forming molybdenum (or tungsten) nitride films.

10) Evaluate Mo$_2$(CF$_3$CO$_2$)$_4$ for spin-on type films to produce molybdenum oxides.

11) Evaluate other metal oxide systems for the deposition of thin film oxides such as Cu-O, W-O, and V-O which have readily available volatile organometallic precursors.

12) Use laser photodeposition of molybdenum oxides as an experimental example of fractal structures grown by diffusion limited growth processes. Pulsed laser deposition allows separation of gas phase and surface
diffusion processes ("sticking" vs. "hopping" effects). Study and model fractal dimensionality which has been shown to be controllable.

13) Perform in situ fluorescence detection using existing triple monochromator and photodiode array in pulsed detection mode to observe fluorescence quenching on the addition of oxygen to the system (for an example of multichannel detection in laser photolysis studies see Lewis et al. [151]).
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APPENDIX A: PHOTOCHEMISTRY CALCULATIONS

Determination of $\sigma_{193}$ for Mo(CO)$_6$

Note: Reflected photons are neglected. This would cause a difference of at most a factor of two (for a perfectly reflecting surface) in calculating $\sigma_{193}$ for Mo(CO)$_6$. The reflectivity of silicon at 193 nm is ~ 63%.

Now back-calculate the absorption cross section at 193 nm from experimentally determined deposit thickness for a standard condition Mo$_4$O$_{11}$ film.

MW of Mo$_4$O$_{11}$ = 560 g/mol (140 g/mol as MoO$_2$.75)

density of Mo$_4$O$_{11}$ = 4.2 g/cm$^3$ = 1.8 x 10$^{22}$/cm$^3$ (as MoO$_2$.75)

"volume" associated with one MoO$_2$.75 = 55.5 Å$^3$ = (3.8 Å)$^3$

# of Mo atoms/cm$^2$ in one layer (as MoO$_2$.75) = 6.87 x 10$^{14}$/cm$^2$

At 3.8 Å per "monolayer" of MoO$_2$.75 experiment deposited

650 Å thick film = 171 "monolayers"

Total molecules deposited/cm$^2$ = (171 x 6.87 x 10$^{14}$/cm$^2$)

= 1.17 x 10$^{17}$/cm$^2$

For 4000 pulses # deposited per pulse (assumed linear)

= 2.9 x 10$^{13}$/cm$^2$ pulse
Assume that the quantum efficiency of 1.
(Number deposited = number of photons absorbed)

Use Beer's law to calculate absorption cross section $\sigma_{193}$.

$$\ln\left(\frac{I_o}{I}\right) = \sigma_{193} c l$$

where $\sigma_{193}$ is cm$^2$, $c$ is concentration is #/cm$^3$ and $l$ is path length cm.

$$\text{photons absorbed} = 2.9 \times 10^{13}/\text{cm}^2/\text{pulse} = I_o - I$$

$$\ln\left(\frac{2.9 \times 10^{16}}{(2.9 \times 10^{16} - 2.9 \times 10^{13})}\right) = \sigma_{193}(2.7 \times 10^{15})(0.2)$$

$$\sigma_{193} = 1.8 \times 10^{-18} \text{ cm}^2$$

estimated error (±0.8 x 10$^{-18}$ cm$^2$)

film thickness ± 10%

concentration x path length ± 20%

photon flux ± 10%

neglecting reflection 0 to -40%

Ozone production

use $\sigma_{193}$ for O$_2$ $4 \times 10^{-21} \text{ cm}^2$, $c_{\text{oxygen}} = 4.1 \times 10^{18} \text{ cm}^3$

Beer's law leads to $I_o - I = 9 \times 10^{13} \text{ O}_3/\text{cm}^2$

$$= 4 \times 10^{14} \text{ cm}^3$$
APPENDIX B: LASER SURFACE HEATING

\[ R_{193} \text{ reflectance Si} = 0.63 \]
\[ \alpha_{193} \text{ abs. coeff.} = 1.6 \times 10^6 \text{ cm}^{-1} (6.2 \text{ nm} = 1/\alpha) \]
\[ (\alpha \text{ is not used in calculation}) \]
\[ \tau \text{ Pulse length} = 1.0 \times 10^{-8} \text{ seconds} \]

**PROPERTIES OF Si**[152]

\[ k \text{ j/(cm s °K)} = (4.184 \text{ j/cal}) \left(\frac{3.64}{T^{1.226}}\right) \]
\[ C_p \text{ j/(g °K)} = (4.184 \text{ j/cal}) \left(0.166(2.375 \times 10^{-4} \cdot T)\right) \]
\[ \rho \text{ g/cm}^3 = 2.32 \]

Surface temperature rise induced by laser pulse for case where absorption length \( \alpha \ll \) conduction length \((2k\tau)^{1/2}\).

\[ \Delta T_{S, \text{peak}} = \left(\frac{2F_o}{k}\right) \left(\frac{\kappa \tau}{\pi}\right)^{1/2} \quad [138] \]

\[ F_o = \text{Radiation absorbed} = \text{incident}(1-R) \]
\[ \kappa = \frac{k}{\rho C_p} \]

**EXAMPLE**

30 mJ/cm² pulse Initial (average) surface temperature 100°C

<table>
<thead>
<tr>
<th>T properties °C</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_S ) rise °K</td>
<td>84</td>
<td>91</td>
<td>98</td>
<td>104</td>
<td>110</td>
<td>116</td>
</tr>
<tr>
<td>( T_S ) peak °C</td>
<td>184</td>
<td>191</td>
<td>198</td>
<td>104</td>
<td>210</td>
<td>216</td>
</tr>
</tbody>
</table>
APPENDIX C: COLLISION FREQUENCIES AND MEAN FREE PATHS

Number of collisions of a single A molecule in Gas B

\[ z_A = \sqrt{2} \frac{\sigma_{AB} c_{AB} N_B}{V} \]
\[ c_{AB} = \frac{(8kT/\pi \mu)^{1/2}}{\mu = m_A m_B/(m_A + m_B)} \]
\[ \lambda_{AB} = \frac{c_{AB}}{2A} \]

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>( N_B ) (#/cm(^3))</th>
<th>( \sigma_{AB} ) (cm(^2))</th>
<th>( c_{AB} ) (cm/s)</th>
<th>( z_A ) (#/s)</th>
<th>( \lambda_{AB} ) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(CO)(_6)</td>
<td>He</td>
<td>1.6 \times 10^{19}</td>
<td>6.5 \times 10^{-15}</td>
<td>1.3 \times 10^5</td>
<td>1.9 \times 10^{10}</td>
<td>6.8 \times 10^{-6}</td>
</tr>
<tr>
<td>Mo(CO)(_6)</td>
<td>O(_2)</td>
<td>4.1 \times 10^{18}</td>
<td>8.0 \times 10^{-15}</td>
<td>5.0 \times 10^4</td>
<td>2.3 \times 10^{9}</td>
<td>2.2 \times 10^{-5}</td>
</tr>
<tr>
<td>Mo(CO)(_6)</td>
<td>Mo(CO)(_6)</td>
<td>2.7 \times 10^{15}</td>
<td>13.3 \times 10^{-15}</td>
<td>1.6 \times 10^4</td>
<td>8.1 \times 10^5</td>
<td>1.9 \times 10^{-2}</td>
</tr>
<tr>
<td>Mo(_{12}) (CO)(_2)</td>
<td>Mo(CO)(_6)</td>
<td>2.7 \times 10^{15}</td>
<td>13.3 \times 10^{-15}</td>
<td>1.6 \times 10^4</td>
<td>8.1 \times 10^5</td>
<td>1.9 \times 10^{-2}</td>
</tr>
<tr>
<td>Mo(_{12}) (CO)(_2)</td>
<td>O(_3)</td>
<td>4.0 \times 10^{14}</td>
<td>13.3 \times 10^{-15}</td>
<td>4.2 \times 10^4</td>
<td>3.1 \times 10^5</td>
<td>1.3 \times 10^{-1}</td>
</tr>
</tbody>
</table>

\* assumed similar to Mo(CO)\(_6\) - Mo(CO)\(_6\) collisions

Note: For a given molecule absorption of a second photon (IF the intensity is high enough for multiphoton processes) would occur on average one half of the pulse length (5 ns) after the first photon. This collision rate (during the laser pulse only) would be \( \sim 2 \times 10^7 \)/s. In this time \( \sim 100 \) collisions with oxygen occur. This, again, indicates that collision and/or reaction with oxygen inhibits fluorescence caused by multiphoton absorption.
Mean Free Paths vs. Distance to Surface

Maximum distance to surface from 2 mm thick reactant gas layer expressed as the number of mean free paths

\[
\begin{align*}
\text{Mo(CO)}_6 - \text{He} & \quad 29000 \\
\text{Mo(CO)}_6 - \text{O}_2 & \quad 9100 \quad (\leq 20\% \text{ O}_2) \\
\text{Mo(CO)}_6 - \text{Mo(CO)}_6 & \quad 10 \\
\text{MoO}_y(\text{CO})_2 - \text{O}_3 & \quad 1.5
\end{align*}
\]

Collisions with Surface

Number of collisions with surface (wall) \[ Z_w = \frac{1}{4} (c_A N/V) \]

where \( c_A \) is \[ (8kT/\pi m_A)^{1/2} \]

\[
\begin{align*}
\text{Mo(CO)}_6 & \quad 1.1 \times 10^{19} \\
\text{MoO}_y(\text{CO})_2^{**} & \quad 5.9 \times 10^{17} \quad \text{(note } 2.9 \times 10^{13}/\text{cm}^2 \text{ deposited per pulse)} \\
\text{O}_2 & \quad 4.8 \times 10^{22} \quad \left( c_A = 4.6 \times 10^4 \text{ cm/s} \right) \\
\text{O}_3 & \quad 1.4 \times 10^{18} \quad \left( c_A = 3.9 \times 10^4 \text{ cm/s} \right)
\end{align*}
\]

**assume same \( c_A \) as \( \text{Mo(CO)}_6 \), initial concentration created by 30 mJ/cm\(^2\) laser pulse is \( 1.45 \times 10^{14}/\text{cm}^3 \).