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Low pressure and plasma enhanced chemical vapor deposition of molybdenum oxide films

Jeffrey Scott Cross
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Low pressure and plasma-enhanced chemical vapor deposition of molybdenum oxide films

Cross, Jeffrey Scott, Ph.D.

Iowa State University, 1992
Low pressure and plasma enhanced chemical vapor
deposition of molybdenum oxide films

by

Jeffrey Scott Cross

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

Department: Chemical Engineering
Major: Chemical Engineering

Approved:

Signature was redacted for privacy.
In Charge of Major Work

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For the Major Department

Signature was redacted for privacy.
For the Graduate College

Iowa State University
Ames, Iowa

1992
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ACKNOWLEDGMENTS

This project could not have been completed without the support of many people. First of all, I would like to thank my advisor, Professor Glenn L. Schrader, for the opportunity to complete this work under his direction. I would also like to thank Professor Schrader for his comments on how to improve my writing and oral presentation skills. I am also indebted to the Department of Chemical Engineering Chairman, Dr. Terry King, and staff, Linda, Peggy and Cindy for their assistance. Previous (Dr. Kurt Olson, Dr. Mark Ekman, Dr. Mark Lashier and Dr. Yu-Neng Chang) and present graduate students in Professor Schrader's research group were also helpful in the completion of this work. I would like to thank Lucy Flanagan, Dr. Michael Columbia and Dr. H. Lu for their assistance in the preparation of this manuscript. The contributions of my committee members: Dr. Steve Martin, Dr. Robert McCarley, Dr. Kurt Hebert, Dr. Thomas Wheelock, and Dr. Maurice Larson were particularly valuable.

I am deeply indebted to Dr. Robert Stephenson for his time, effort, and instructions in the use of experimental design. The profilometry measurements on the film thickness were provided by Mr. Alan Landon of the Microelectronic Research Center and were truly appreciated.

I would like to give a special thanks to my parents, Jim and Kathy Cross and siblings, Julie, Jeanne and Jay; for their support.

Finally, I would like to thank the Phillips Petroleum Corporation for providing the financial assistance which supported me through my four years at Iowa State University.
GENERAL INTRODUCTION

Explanation of Dissertation Format

This dissertation consists of two papers each written in a form suitable for publication in a technical journal. A general introduction precedes the two papers to orient the reader to the scientific relevance of this work. After each of the papers is an appendix. An overall summary with recommendations for future research follows the second paper. References cited in the general introduction and summary are given at the end of the dissertation.

Introduction

In recent years, chemical vapor deposition (CVD), has gained considerable interest as a fabrication technique to produce films of diamond, superconductors, and semiconductors. CVD is a vapor technique where a material is produced by a chemical reaction from a gaseous precursor, ultimately depositing a solid phase on a substrate. The energy for activating the chemical reaction can be provided thermally, electrically (plasma or discharge) or by photons. For a plasma process, a discharge is created by excitation of the gas phase by a radio-frequency (RF) or microwave field. The presence of the plasma in the deposition process acts as a catalyst to reduce the energy of activation for the film forming reaction.

Recently, interest in plasma enhanced chemical vapor deposition (PECVD) has increased due to lower substrate temperature requirements for microelectronic devices. Most of the published research using PECVD has focused on producing Si, GaAs or other materials
used in the electronics industry. PECVD is sometimes compared to low pressure chemical vapor deposition (LPCVD) which relies on thermal activation but is conducted at conditions similar to PECVD. Little fundamental research has been reported on using PECVD or LPCVD to produce non-Si materials, particularly refractory metal oxides.

Refractory metal oxides have uses as catalysts in their powder form, or as potential chemical sensors, solar cells and display devices when prepared as a film. Powders of molybdenum oxides have been prepared and extensively characterized by numerous researchers. Preparation of thin films of molybdenum trioxide, MoO₃, has been limited primarily to physical vapor deposition and atmospheric chemical vapor deposition. There is little published information available on the preparation of molybdenum trioxide films using either LPCVD or PECVD. This study was undertaken to develop a system to produce this material and gain an understanding of how it forms using LPCVD and PECVD processes.

The goal of this proposed research is to provide new fundamental information about the formation of thin films of molybdenum trioxide from molybdenum hexacarbonyl and oxygen using plasma enhanced and low pressure chemical vapor deposition. Both deposition systems are very complex, with numerous processes occurring simultaneously. However, it is thought that by carefully controlling the process parameters such as deposition temperature, the gas phase composition (reactant Mo(CO)₆/O₂ ratio), RF power density, and system pressure, insight can be gained into the deposition process. New fundamental information concerning the deposition process would lead to improved thin film synthesis of metal oxides as well as other layered compounds.
Literature Review

This section contains a review of the literature related to the preparation techniques for producing molybdenum oxides. The section is divided into two parts. The first part covers the bulk structure and characterization, and the second part covers the thin film preparation.

Structure and characterization of bulk phases

The principal stable oxides of molybdenum are MoO₂ and MoO₃. Many metastable shear structures of molybdenum oxide exist between MoO₂ and MoO₃, and they have the general stoichiometry of Mo₉O₉₊₂, where y = 4, 5, 8, 9. The phase diagram shown in Figure 1 also indicates the physical state of these compounds as function of oxygen concentration and temperature. The physical properties (resistivity, melting point, crystal structure, etc.) of the molybdenum oxide compounds vary as a function of their oxygen content. Molybdenum dioxide melts at 2600°C and molybdenum trioxide melts at 800°C.

There are two crystalline polymorphs of MoO₃, α and β. The basic building block for both α and β is the MoO₆ octahedron as shown in Figure 2. α-MoO₃ (which will be referred to as MoO₃) has a unique layered structure held together by van der Waals forces; oxygens in the octahedron are shared by one, two or three molybdenum atoms depending upon their location in the layered structure (see Figure 2a). α-MoO₃ is readily characterized using XRD, XPS, laser Raman and infrared spectroscopy. β-MoO₃ has a ReO₃ structure with each oxygen being shared by two molybdenum atoms (see Figure 2b). The metastable β-phase decomposes into the stable α-phase upon heating to temperatures between 300-350°C.
Figure 1 Mo-O phase diagram

Figure 2 MoO₃ a) α and b) β structures
The transformation can be followed using XRD or Raman spectroscopy. Table I lists the principal vibrational frequencies for molybdenum oxides using Raman spectroscopy.

Analysis of molybdenum oxide powders has shown that they possess unique properties for photochromic and electrochromic applications. These properties can be better utilized when the materials are in the form of a thin film. Synthesis of films of molybdenum oxide using various techniques are discussed in the following section.

Thin films

CVD general overview. CVD is a process in which a gaseous precursor molecule reacts to form a solid on a substrate (Figure 3). The process is complex with many things occurring simultaneously. Insight into the deposition process is provided by examining the deposition fundamentals.

The fundamental principles of CVD are based on chemistry, thermodynamics, reaction kinetics, transport phenomena and film growth. Most of the work dealing with fundamental studies in CVD has been completed on Si, SiO₂, Si₃N₄, W and GaAs because these materials are used in integrated circuits. From this work, it is possible to generalize the results to different chemical systems but due to inherent differences between systems and products, gaps in understanding are best clarified through theoretical and empirical results.

Before actually producing CVD films, CVD experts advocate the use of thermodynamics to determine if the desired product is stable. Thermodynamics not only facilitates a better understanding of the process but also provides an efficient method for optimizing the parameter settings. Analysis of a particular process can be conducted using
Table I Comparison of molybdenum oxide Raman spectra from 1000 to 150 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>MoO(_2)(^a)</th>
<th>(\gamma)-MoO(_{11})(^a)</th>
<th>(\eta)-MoO(_{11})(^a)</th>
<th>(\beta)-MoO(_3)(^{ab})</th>
<th>(\alpha)-MoO(_3)(^a)</th>
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<tr>
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<td>157 s</td>
</tr>
</tbody>
</table>

s-strong, m-medium, w-weak, v-very, sh-shoulder

a-ref. 8, b-ref. 7
Figure 3 Schematic of chemical vapor deposition process
an IBM i386 PC with a math co-processor, thermodynamic data, and a computer program, Solgasmix-PV\textsuperscript{12}. The program, Solgasmix\textsuperscript{13}, was originally written to calculate equilibria in multiphase systems by the direct minimization of system free energy. It was modified by Besmann\textsuperscript{12} using the ideal gas law to calculate thermodynamic equilibrium at a constant total gas volume with variable total pressure.

Although thermodynamics provides a method to determine process variable settings under equilibrium conditions, most CVD systems operate under non-equilibrium conditions. Hence, it becomes important to consider other factors when depositing films such as reaction kinetics, transport phenomena and film growth.

Transport phenomena have pronounced influences on the performance of CVD reactors\textsuperscript{14-16}. Computational fluid dynamics is frequently used to model fluid and thermal profiles in CVD reactors. The models have helped in the development and understanding of the deposition process. Theoretical models have concurred with experimental results that gas flow and thermal profiles affect deposit rate, uniformity, and composition\textsuperscript{15-17}.

CVD process variables The decomposition of a precursor and subsequent steps to form a film are controlled by the process variables: temperature, pressure, gas composition, and flow rate (other process variables relating to glow discharges will be discussed in the following section). For thermally activated CVD systems it is the temperature that drives the reactions and film growth. This is exemplified by examining the results of a Si deposition system as a function of precursor concentration and temperature\textsuperscript{18} (Figure 4).

A plot of Si film growth rate versus temperature exhibits three regions (Figure 4). In regime a, at high temperature and high precursor concentrations, the growth rate is temper-
Figure 4 Variation in silicon growth rate versus temperature and concentration

ature dependent. In this regime, the precursor partially decomposes in the gas phase and deposits on the chamber walls reducing the deposition rate. This is also called homogeneous gas phase nucleation and has been observed for metal carbonyls as well.

In regime b, the growth rate is independent of temperature and linearly dependent on the precursor concentration. In this regime the growth rate is controlled by mass transfer effects of the precursor diffusing through the boundary layer to the substrate surface. The thickness of the boundary layer is a function of the pressure, gas velocity and flow rate.

For regime c, the growth rate is limited by reaction kinetics and hence controlled by the substrate temperature and precursor concentration or supersaturation. Films deposited
under these conditions are plagued by poor crystallinity and incorporation of by-products into the deposit.

In order to form a crystalline deposit, the structure of the deposited material depends on the temperature and supersaturation\textsuperscript{21} (Figure 5). Species absorbed on the substrate surface have to have sufficient energy and time for reaction and surface diffusion before they are covered by subsequent impinging species (Figure 3 and 5). Otherwise, the deposits are amorphous which occurs at low substrate temperature and high precursor concentrations\textsuperscript{9,21}.

CVD and other techniques for producing Mo, and MoO\textsubscript{y} films One method of producing molybdenum and molybdenum oxide films is by the thermal decomposition of Mo(CO)\textsubscript{6}, MoCl\textsubscript{5} or MoCl\textsubscript{2}O\textsubscript{2}. Some of the earliest refractory metal plating was done with metal halides. However, the by-products of the deposition, notably HF and HCl, are both extremely toxic and corrosive. Thus, metal carbonyls appear to be more attractive because of their less corrosive nature. They also have vapor pressures between 0.1 and 0.5 torr at room temperature, and decompose at moderate temperatures of 100 to 200°C.
Lander and Germer\textsuperscript{19} performed some of the early work with hexacarbonyl decompositions at temperatures of 350 to 775°C to produce molybdenum, tungsten and their oxides and sulfides. The following reactions were thought to be important for the Mo deposition:

\begin{equation}
\text{Mo(CO)}_6 \rightarrow \text{Mo} + 6\text{CO}
\end{equation}

\begin{equation}
2\text{CO} \rightarrow \text{C} + \text{CO}_2
\end{equation}

\begin{equation}
\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2
\end{equation}

The focus of their research was to produce Mo and W films, thus, their molybdenum oxide work was limited.

Numerous investigators have since produced Mo films from molybdenum hexacarbonyl\textsuperscript{19,22,23}. One of the problems encountered by the above investigators was oxygen and carbon contamination of the film. Lander and Germer investigated this problem by adding H\textsubscript{2}O to the gas stream to reduce the carbon content of the deposited film\textsuperscript{19}. Water vapor was found to decrease the carbon content when the substrate temperature was above 500°C. Higher substrate temperatures without H\textsubscript{2}O and above 550°C, were also found to give low-carbon films. However, the films were of poor quality due to gas phase nucleation at deposition temperatures > 400°C.

A second precursor, MoCl\textsubscript{4}, was used to produce Mo films according to the following reaction\textsuperscript{25-28}:

\begin{equation}
\text{MoCl}_4 + 2.5 \text{H}_2 \rightarrow \text{Mo} + 5 \text{HCl}
\end{equation}

The above reaction does not require an annealing step to reduce contaminants but must be carried out at higher temperatures, 500-800°C\textsuperscript{28}, to obtain high quality Mo films.
Within the past 10 years, depositions of MoO$_2$ and MoO$_3$ films from Mo(CO)$_6$, MoCl$_5$ and MoO$_2$Cl$_2$ have shifted towards the synthesis of films for potential solar cells and electrochromic displays. Mo(CO)$_6$ has been used as the precursor to synthesize both MoO$_2$ and MoO$_3$ films$^{4,29,30}$. A general reaction for the MoO$_2$ depositions process is

$$\text{Mo(CO)}_6 + O_2 \rightarrow \text{MoO}_2 + 6\text{CO} \quad (5)$$

Most of the films were used in solar cell tests so little chemical analysis of the film was reported$^{4,29,30}$. The deposition conditions for MoO$_2$ were similar to those for the deposition of Mo, atmospheric pressure and a substrate temperature between 300 - 400°C, except that an oxygen stream was added to the carrier gas. Higher substrate temperatures were not attempted because of gas phase nucleation$^{34}$.

Oriented films of MoO$_3$ were produced$^4$ by annealing an atmospheric CVD MoO$_2$ layer in air and oxygen at 500 and 600°C according to the following reaction,

$$\text{MoO}_2 + 1/2 \text{O}_2 \rightarrow \alpha-\text{MoO}_3 \quad (6)$$

X-ray diffraction spectra revealed a polycrystalline film with a preferred (0k0) orientation of MoO$_3$ in an orthorhombic form. The physical properties of the film were found to vary with the annealing conditions and film thickness.

MoO$_2$ films were produced from the pyrolytic hydrogen reduction of MoO$_2$Cl$_2$ in a temperature range of 550 - 700°C$^{31}$. A post annealing step was not necessary since carbon was not present in the system. Varying the substrate temperature directly affected the oxygen content of the film. At substrate temperatures below 630°C the films were oxygen rich; above this temperature the films were Mo rich.
A general review of the plasma deposition process is contained in the following section in addition to a review of the work on Mo, MoO\textsubscript{y} and MoO\textsubscript{3} films produced by plasma processing.

**Plasma deposition** The complexity of plasma processing is illustrated by Figure 6 which shows the numerous parameters involved in the process and how these variables interact to produce a film. PECVD processes utilize collisions of charged species in the gas phase and to a lesser degree the thermal energy of the substrate to drive chemical reactions that produce films of material. The charged species are created by an electric field generated by a DC, RF or MW source depending upon the product desired.

The plasma process is initiated by electrons being accelerated in an electric field and colliding with atoms or molecules typically at pressures between 10\textsuperscript{-3} and 10 torr. The average electron energy is 2 eV\textsuperscript{22}. Most of the collisions are elastic where the electron changes direction and no energy is exchanged. It is the inelastic electron collisions between molecules and electrons that generate ions and excited species\textsuperscript{32}. Degeneration of the excited species, which is accompanied by a photon emission, give plasmas their characteristic glow.

A distinguishing characteristic of PECVD over thermal CVD is that the surface of the growing film is frequently bombarded by charged species from the gas phase. An electrically isolated substrate placed inside a plasma typically builds a negative charge with respect to the discharge. The potential difference between the plasma and the isolated substrate accelerates ions to the surface\textsuperscript{32}. The bombardment of the surface with ions increases the film density, stress, and film adhesion particularly at low substrate temperatures. Ion bombardment gives the adatoms (atoms from the gas phase adsorbed to the surface) sufficient
Figure 6 Interaction complexity of homogeneous plasma processes that determine film properties in PECVD
energy for surface diffusion and chemical reaction. Thus, ion-surface interactions present in a plasma decrease the dependency of the film morphology and microstructure on substrate temperature.

The frequency of the generator has been shown to influence the deposition and etching of films. Most commercial plasma apparatus operate at 13.56 MHz because this is an FCC licensed industrial frequency. High RF and microwave frequencies have been shown to more effectively transmit energy into the plasma and produce greater ionization. The high ion concentration can also lead to film bombardment and etching of the deposits. Although some film bombardment increases surface diffusion, too much can lead to high film stress. Thus, researchers have concluded that the use of low frequency RF sources (450 kHz) can lead to higher quality plasma deposited silicon dioxide films.

One aspect of plasmas that leads to their non-equilibrium behavior is that different species in the plasma have different energy levels or temperatures as shown in Figure 7 for a cold plasma. Electrons are the hottest species in the plasma with temperatures on the order of 20,000°K. Collisions between the hot electrons and gas molecules provide plasmas with their unique chemistry.

Film formation from plasma deposition can be viewed as a series of elementary steps. The process is initiated by the collision of a precursor gas molecule with an energetic electron. If the collision is inelastic, the precursor may dissociate into either a neutral or a charged radical (ion). These radicals may react in the gas phase and then diffuse to the substrate surface. The species that arrive at the surface may bond to the substrate and react to form the product. The activation energy to form the product can be provided by a temper-
Figure 7 Typical values for species in a glow discharge.32

ature activated surface reaction or from bombardment of the surface with energetic radicals and electrons. Researchers are now beginning to address the fundamental concepts of film formation using PECVD. PECVD processes for formation of films of refractory metals, metal oxides and Si compounds are discussed in the following section.

Fundamental investigations into the plasma chemistry of oxygen have been undertaken using optical emission spectroscopy (OES) and mass spectroscopy (MS). Aita and Marhic36 investigated the interaction of argon and oxygen in a RF glow discharge on the formation of
zinc oxide. They found that neutral oxygen in an excited, repulsive state, \( O_2^+ \), dissociated into atomic oxygen. The dissociated oxygen products increased the relative rate of zinc oxide film growth.

Plasma chemistry has been researched for over 60 years, however, it was not until the last 20 years that it has been applied to producing thin films. The most extensively studied plasma processes are Si\(_2\)O and Si\(_3\)N\(_4\) film deposition and etching\(^{37}\). Controlling the PECVD process variables such as temperature, plasma power density, gas composition, and pressure are essential for film formation, growth and reproducibility.

Recently, workers\(^{38,39}\) have focused on understanding the important parameters of the Si\(_2\)O process. Lucovsky used a remote PECVD process where he selectively excited specific gas reactants and neutral species\(^{38}\). The primary surface reactants were metastable \( O_2^+ \) and neutral SiH\(_4\) as determined by optical emission and mass spectroscopy. They also reported that the remote PECVD films, deposited at substrate temperature less than 500°C, had similar film properties to the thermally grown Si\(_2\)O films at 1000°C.

Another plasma system was used to study the influence of four process parameters on the formation of SiNH films\(^{40}\). Since plasma deposition is a non-equilibrium process, various stoichiometries of Si to N films were produced. Bohn and Manz determined that the gas SiH\(_4\)/NH\(_3\) ratio and RF power had the greatest response on thin amorphous SiNH films\(^{40}\).

A comparison study on the deposition of W from H\(_2\)-WF\(_6\) using LPCVD and PECVD investigated the effect of plasma surface interactions on nucleation and film growth\(^{41}\). Two different phases, \( \alpha^- \) and \( \beta^- \), of elemental tungsten films were grown. The growth of a
particular phase was a function of the $H_2/WF_6$ gas ratio in the system. The PECVD system films had increased crystallinity which was attributed to higher effective surface temperatures (enhancing surface diffusion) resulting from the plasma-surface interaction.

Ianno and Plaster\textsuperscript{42} and Okuyama\textsuperscript{43} produced molybdenum films from molybdenum hexacarbonyl by PECVD. Ianno's system consisted of a parallel plate reactor with a temperature controlled lower electrode, driven by a 13.56 MHz capacitively coupled RF generator in parallel with a d.c. power supply. The deposition occurred on SiO$_2$ films with a system pressure of 80 mtorr. A second gas, either H$_2$ or Ar, was added to the Mo(CO)$_6$ vapor to stabilize the plasma because using only Mo(CO)$_6$ vapor in the chamber produced an unsustainable discharge. Ianno produced amorphous molybdenum films from Ar-Mo(CO)$_6$ vapor\textsuperscript{42}. The films contained some MoO$_3$, Mo$_3$O$_{11}$ and carbon before and after annealing\textsuperscript{42}. XRD analysis of the as-deposited films of H$_2$ and Mo(CO)$_6$ vapor contained carbon and oxygen (in the form of hydroxide). Using hydrogen as the carrier gas during the deposition helped to reduce the films upon annealing, leaving carbon but no oxygen. Okuyama’s semi-amorphous films were prepared using a simple parallel plate diode chamber filled with Mo(CO)$_6$ vapor to 0.1 or 0.2 torr\textsuperscript{43}. The deposited films on glass were of uneven thickness, with the center thicker than the edges. The deposited films contained 20 - 30 % carbon but no oxygen as analyzed from X-ray microanalysis.

R.F. plasma reactive sputtering was used to fabricate polycrystalline MoO$_3$\textsuperscript{7} and MoO$_x$ films\textsuperscript{44}. Four types of MoO$_3$ films were produced: amorphous, a metastable $\beta$-phase, an oriented $\alpha$-phase and a mixed $\alpha/\beta$-phase\textsuperscript{7}. X-ray diffraction of the $\alpha$-films revealed that the films grow with their (0k0) basal planes parallel to the substrate surface. Jankowski and
Schrawyer deposited MoO<sub>y</sub> films of various stoichiometries and crystallinity by varying the target power and controlling the deposition rate.<sup>44</sup>

Tracy and Benson<sup>45</sup> prepared amorphous electrochromic tungsten oxide and molybdenum oxide films by plasma-enhanced chemical vapor deposition from WF<sub>6</sub>, W(CO)<sub>6</sub> and Mo(CO)<sub>6</sub> vapor and oxygen. The films were produced in a 300 W, electrodeless, 13.56 MHz radio frequency (RF) capacitive discharge by co-feeding WF<sub>6</sub> or metal carbonyl vapor and oxygen. The amorphous films were deposited on glass or on films of indium tin oxide upon glass substrates. The deposition temperature was between 50 and 65 °C as measured by a thermocouple. The system pressure was between 19 and 133 Pa (0.142 and 1 torr). The gas feed ratio of the metal precursor to oxygen was between 0.5 and 5.1 and the deposited films were between 1500 and 4000 Å thick. When the Mo(CO)<sub>6</sub>/O<sub>2</sub> ratio was high, the deposited MoO<sub>y</sub> film had a brown or black appearance typical of a reduced molybdenum oxide. The dark films were then exposed to an oxygen plasma, and the color of the film changed to white or transparent. Neither the actual stoichiometry nor the chemical analysis of the molybdenum oxide films were determined. Auger spectroscopy of a WO<sub>y</sub> film revealed K, C, and N peaks in the Auger spectrum.

Statistical experimental design

To study the deposition in a way that allows for the process variables influence on the deposit to be quantified, a designed experimental approach was used for results in both papers. Experimental design allows for the process to be modeled using an empirical
mathematical function. The model can be linear, quadratic or cubic depending upon the particular response.

This method is used in the chemical process industry for optimizing complex chemical processes but it is also well suited for chemical vapor deposition. A statistical approach is appropriate for CVD because the process is very complex and data does not exist for the development of a mechanistic model.

The use of experimental design in CVD processes has been limited. In 1991, a literature search of the Chemical Abstracts using "experimental design" and "film" as keywords yielded one reference on diamond CVD. Another experimental design reference was found on PECVD and was reviewed on page 17. Recently, three articles have appeared on the use of experimental design using LPCVD for tungsten and silicon nitride films. Both Si$_3$N$_4$ research groups were able to model the process and determine which variable had the greatest effect on several responses.

There are numerous designs to consider when selecting an experimental design: factorials (fractional, $2^n$ or $3^n$), response surfaces, and Taguchi methods. The design chosen depends upon the goal of the researcher. One particular general design which allows for the assessment of quadratic terms is a central composite design (Figure 8). For both two and three variable systems, the design itself consists of three portions: a square or cube portion, star or axial points and a center point. The design can contain two - six variables but as the variables increase above three; it becomes difficult to visualize the system graphically.
Figure 8 Central composite designs with (a) two and (b) three factors.50

Factorial designs offer several advantages over traditional one factor at a time (OFAT) or one dimensional experimentation. For a two level design the main effect a variable has on a response can be quantified according to

\[
Main \, effect = \frac{\Sigma R_1}{2} - \frac{\Sigma R_2}{2}
\]  

(7)

where \(R_1\) and \(R_2\) are the response at levels 1 and 2. This type of analysis can be used for all the parameters for a two level design to determine which are significant.50

Interactions between parameters are observed when the settings of one parameter influence the response relative to another parameter. For a two parameter system operated
at two levels, variables that interact strongly are indicated by intersecting lines whereas those that do not interact have parallel lines (Figure 9).

Factorial designs are also more efficient than OFAT$^{50,51,53}$. The efficiency increases with the number of factors considered. For a four variable design compared to a OFAT for four variables, the design method is 2.5 times as efficient$^{50}$.

Figure 9  Process variables with a) no interaction b) with interaction$^{50}$

Summary

Although research has been reported on the synthesis of MoO$_3$ from Mo(CO)$_6$ as a two step atmospheric CVD process, that is, deposition followed by an annealing step in oxygen or air, limited results are reported producing polycrystalline MoO$_3$ films using LPCVD$^{19}$. One study reported using Mo(CO)$_6$ focused on producing Mo films under LPCVD conditions. Depositing films of $\alpha$-MoO$_3$ using LPCVD compared to atmospheric CVD has several advantages including less gas phase nucleation, reduced by-product contamination and simplicity of a single step process.
PECVD results suggest that RF power and gas composition are the most important variables for film formation. PECVD appears to be an attractive thin film technique for producing crystalline MoO₃ films due to its lower substrate temperature. Little fundamental research has been reported on the synthesis of crystalline MoO₃ films using either LPCVD or PECVD.

Finally, CVD analysis using experimental design offers several advantages over traditional experimentation. The results are valid over a range of conditions and not at one particular variable setting. This approach appears to be well suited for modeling the CVD process and for comparing LPCVD and PECVD systems on α-MoO₃ formations.

Research Objective

It is the objective of this research to investigate the formation of crystalline molybdenum trioxide films from Mo(CO)₆ and O₂ using low pressure and plasma enhanced chemical vapor deposition. This investigation will attempt to identify the important process parameters that lead to molybdenum trioxide and compare the results with thermodynamic equilibrium calculations. The formation mechanisms for the two types of processes will be addressed. Fundamental insight into the formation of layered crystalline molybdenum oxide system is the ultimate goal of this research.
PAPER 1

LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF MOLYBDENUM OXIDES FROM MOLYBDENUM HEXACARBONYL AND OXYGEN
ABSTRACT

Thin films of molybdenum oxides were deposited at 300-500°C and 200-1014 mtorr from Mo(CO)$_6$, O$_2$ and H$_2$O using an inductively heated low pressure chemical vapor deposition (LPCVD) system. Two oxygen gas flow rates of 5 and 15 sccm were used. $\alpha$-MoO$_3$ films were deposited at temperatures of 425°-450°C, at 660-1014 mtorr with an O$_2$ flow rate of 15 sccm and at 450-500°C and 300-500 mtorr with an O$_2$ flow rate of 5 sccm. The polycrystalline films were deposited on silicon (100) wafers and exhibited preferred orientations. Gas phase decomposition of the precursor was significant with temperatures > 400°C and pressure > 600 mtorr with an O$_2$ flow rate of 15 sccm. Due to decomposition of the precursor in the gas phase and low gas velocities, the films decreased in thickness in the direction of flow. Thermodynamic equilibrium calculations indicated that MoO$_3$ is the most stable phase for all the deposition conditions. However, $\alpha$-MoO$_3$ was deposited only at high temperatures and pressures. A quadratic model of $\alpha$-MoO$_3$ formation was developed using experimental design for the 5 sccm depositions as a function of temperature and pressure. Both parameters were significant in the formation of $\alpha$-MoO$_3$. The films were characterized using X-ray diffraction and X-ray photoelectron, Auger, and laser Raman spectroscopies.
1 INTRODUCTION

Molybdenum oxides include phases such as MoO₂, MoO₃, and several "shear structures" MoₓOₙ₋₁, where y = 4, 5, 8, and 9. Solid state preparation of MoₓOₙ₋₁ shear structures typically is performed by mixing stoichiometric amounts of MoO₂ and MoO₃ in sealed ampules and heating at 500 - 870°C for two days to several weeks. Important physical properties of the molybdenum oxides such as resistivity and melting point vary as a function of the oxygen content. Although much previous work has emphasized bulk materials, thin films of molybdenum oxide are also of interest. Potential applications for MoO₂ have focused primarily on solar cells. MoₓOₙ₋₁ materials have been studied because of low-dimensional conductivity and optical anisotropy. Treated, amorphous MoO₃ films have recently achieved attention because of photochromic and electrochromic properties which could be useful in display or memory devices. MoO₃ has also been studied extensively because of its catalytic activity.

Crystalline MoO₂ and MoO₃ films can be prepared by thermal oxidation of Mo metal, by chemical vapor deposition (CVD), and by exfoliation. These techniques rely upon thermal oxidation at 470-680°C in order to transform the starting materials [Mo₆, MoO₂ and MoS₂] to produce polycrystalline α-MoO₃. Reactive sputtering can be used to produce molybdenum oxides with different stoichiometries (MoₓOₙ, MoO₂, and MoO₃). Synthesis of the molybdenum oxide films using CVD has several advantages: synthesis time may be reduced and CVD can produce better step coverage compared to line-of-sight processes such as sputtering or evaporation. Previous CVD research has focused
primarily on producing molybdenum oxide films from molybdenum halides or molybdenum hexacarbonyl. Lander and Genner\textsuperscript{12} performed pioneering work on low pressure CVD using Mo(CO)$_6$; Mo films were produced primarily. Preparation of MoO$_3$ films using atmospheric CVD from Mo(CO)$_6$ has been accomplished in a two step process\textsuperscript{8}. MoO$_2$ films were deposited at 300°C and then oxidized at 500 or 600°C. The films were characterized by XRD and optical properties were evaluated. Molybdenum oxides have also been produced from Mo(CO)$_6$ via laser-assisted CVD. Olson and Schrader\textsuperscript{13} employed an ArF excimer laser to produce polycrystalline Mo$_4$O$_{11}$ (< 1000Å). Amorphous molybdenum oxide films for electrochromic applications were produced via plasma enhanced CVD\textsuperscript{14}. The molybdenum oxygen stoichiometry of the light gray deposits was not determined.

The present study was undertaken to produce polycrystalline MoO$_3$ films from Mo(CO)$_6$, O$_2$ and H$_2$O using LPCVD, and to determine the effect of temperature, pressure and precursor flow rate on the deposits. Evaluation of the process variable influence on molybdenum oxides will ultimately lead to a better understanding of the deposition process.
2 EXPERIMENTAL EQUIPMENT AND METHODS

2.1 Deposition Equipment

The films were prepared using a LPCVD chamber as depicted in Figure 1. The quartz chamber was surrounded by an induction coil which was connected to a 5 kW Lepel, 200 - 450 kHz, RF generator. The generator heated an electrically isolated, SiC coated graphite susceptor; no discharge was observed. Feed mixtures of Ar (99.995 %, Matheson), O₂ (99.97 %, Matheson), Mo(CO)₆ (99 %, Alfa), and water vapor were used. The O₂ to Mo(CO)₆ molar ratio in the gas stream was regulated by varying the quantity of gas flowing through a Mo(CO)₆ sublimator maintained at 30°C. The concentration of Mo(CO)₆ in the gas phase...
was determined by collecting the vaporized precursor in a cold trap after the sublimator and correlating the mass of the sublimed Mo(CO)$_6$ with gas flow rate. Brooks mass flow controllers were used to regulate the flow rate of oxygen and argon. The pressure in the system was measured with an MKS capacitance manometer and regulated by throttling a bellow valve located in the roughing pump intake line. Water vapor could be supplied to the chamber from a liquid water reservoir maintained at 0°C. A UTI 100C mass spectrometer with an ISS-325 sampling system were used to analyze the effluent.

2.2 Characterization

The deposited films were characterized with a Nicolet 60SX Fourier transform infrared spectrometer, Spex Triplermate laser Raman spectrometer, PHI scanning Auger electron spectrometer, PHI 5300 ESCA system, Siemans X-ray diffractometer (XRD), a JEOL scanning electron microscope (SEM), and a Tencor alpha step profilometer.

2.3 Experimental Methods

Prior to film depositions, the sample and susceptor were heated to 600°C using the RF generator; evacuation by a turbomolecular pump produced a pressure of 8 x 10$^{-4}$ torr. The substrates were 3" silicon (100) wafers; no attempt was made to remove surface oxide. The RF generator power was adjusted to achieve a susceptor temperature of 300-500°C. The carrier gas was then admitted into the chamber for one hour prior to deposition. After the desired deposition time (20 and 70 minutes), Ar was used to purge the chamber while the sample/susceptor was allowed to cool to room temperature.
Films were deposited at O\textsubscript{2} gas flow rates of 5 and 15 sccm (sccm=standard cm\textsuperscript{3}/min) using both a one factor at a time (OFAT) deposition routine and statistical experimental design. Ranges of temperature, pressure, and Mo(CO)\textsubscript{6} flow rate for the 15 sccm depositions are listed in Table I. The methodology used to compare the influence of process parameters on the deposit was to vary one variable while holding the other two constant. This coincided with depositing films with a Mo(CO)\textsubscript{6} flow rate of 4.5 mg/min, at a pressure of 660 mtorr while varying the temperature from 300 - 450°C and at 425°C while varying the pressure from 217 - 1014 mtorr. Two levels of Mo(CO)\textsubscript{6} flow rate (2.3 and 4.5 mg/min) were used at 425°C and 470 mtorr.

Ten films were deposited at an O\textsubscript{2} flow rate of 5 sccm using a two factor (temperature and pressure) two level central composite design\textsuperscript{15} (Table II). The ranges of temperature and pressure investigated were from 425-500°C and 200-500 mtorr.

For both gas flow rates three responses were recorded including deposition rate, the gas phase CO-CO\textsubscript{2} ratio, and α-MoO\textsubscript{3} content of the deposits. The deposition rate was determined by weighing the films before and after the deposition and dividing the difference by the deposition time. The gas phase CO-CO\textsubscript{2} amp signal ratio was determined by dividing the mass spectrometer mass to charge signal at 28 by the signal at 44. This ratio was reported because the actual signals change with pressure. A model was developed of the α-MoO\textsubscript{3} content from characterization of the deposits and by measuring the α-MoO\textsubscript{3} surface coverage of the deposits. The contribution of temperature and pressure to the model was determined by standardizing the variables according to the following equations.
Table I Summary of deposition conditions for oxygen flow rate of 15 sccm

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ flow rate (sccm)</td>
<td>15</td>
</tr>
<tr>
<td>O₂/Mo(CO)₆ molar ratio</td>
<td>25-61</td>
</tr>
<tr>
<td>Water flow rate (sccm)</td>
<td>0.0-0.15</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>300-450</td>
</tr>
<tr>
<td>Pressure (mtorr)</td>
<td>265-1014</td>
</tr>
</tbody>
</table>

Table II Deposition conditions used for experimental design with oxygen flow rate at 5 sccm

<table>
<thead>
<tr>
<th>Process Variables</th>
<th>Levels</th>
<th>Increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mtorr)</td>
<td>(200, 300, 400, 500)</td>
<td>100</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>(425, 450, 475, 500)</td>
<td>25</td>
</tr>
<tr>
<td>Mo(CO)₆ flow rate (mg/min)</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>O₂ flow rate (sccm)</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

ap - axial point  
scmm = standard cm²/min

cp - center point

\[
X_T = \frac{(Temp - 450)}{450} \quad (1) \quad X_P = \frac{(Press - 300)}{300} \quad (2)
\]

The t-statistics were calculated for each of the coefficients according to a t-distribution and the following expression

\[
t = \frac{\bar{Y} - u_o}{s/\sqrt{n}} \quad (3)
\]

where \( \bar{Y} \) is the variable average, \( u_o \) is the mean, \( s \) is the standard deviation and \( n \) is the number of observations. The model was developed using regression analysis with SAS® 16, a statistical software package.
3 RESULTS

Films were deposited at flow rates of 5 and 15 sccm of oxygen. The results of the films deposited at 15 sccm are presented in section 3.1 and at 5 sccm are presented in section 3.2 and 3.3.

3.1 Process Variables at 15 sccm O₂

3.1.1 Temperature effects

The deposition temperature influenced the stoichiometry, morphology and deposition rates of the films. Laser Raman spectroscopy revealed that films deposited at 425-450°C had strong bands at 996, 819, 666, 521, 337, 284, and 157 cm⁻¹ (Figure 2). These films were an identical match to α-MoO₃ except an addition peak at 521 cm⁻¹ which is attributed to the Si wafer. Auger spectroscopy of the MoO₃ films indicated that the deposits contain less than 1 % C. ESCA analysis of the film determined that the Mo 3dₓ/₂ and 3dₚ/₂ electrons had binding energies of 232.7 and 235.9 eV respectively. These values are in close agreement with Mo(VI) binding energies of 232.6 and 235.8 eV reported in the literature for MoO₃\textsuperscript{17}. XRD analysis (Figure 3) identified the light gray deposits as α-MoO₃; the most intense peaks are at 6.88, 3.46 and 2.31Å which correspond to (020), (040) and (060) planes of α-MoO₃. Films deposited at 425-450°C had a columnar structure and faceted surface (Figure 4). As the film temperature decreased, the structure, composition, and crystallinity of the films changed (see Appendix A Figures A1 and A2) and the deposition rate increased (Figure 5).
Figure 2  Raman spectra of (a) \( \alpha \)-MoO\(_3\) powder and (b) film deposited at 425\(^\circ\)C and 670 mtorr

Figure 3 XRD pattern of film deposited at 425\(^\circ\)C and 670 mtorr
Figure 4  SEM micrograph of surface of α-MoO₃ film deposited at 425°C and 670 mtorr

Figure 5  Deposition rate versus temperature at a pressure of 660 mtorr with a Mo(CO)₆ flow rate of 4.5 mg/min
3.1.2 Pressure effects

The deposition pressure strongly influenced deposition composition and uniformity. Films deposited at 425°C consisted of reduced molybdenum oxides (see Appendix A Figure A3) at pressures < 400 mtorr, mixed phases with pressures between 400 - 600, and α-MoO₃ with pressures > 600 mtorr. At intermediate values of pressure, 370 to 470 mtorr, the deposits consisted of mixed molybdenum oxides and α-MoO₃. These films had the reduced material nearest the gas inlet and α-MoO₃ on the trailing edge of the deposit (Figure 6). The α-MoO₃ content of these films could be increased by decreasing the Mo(CO)₆ concentration of the gas from 4.5 to 2.3 mg/min which corresponded to a lower deposition rate. The deposition rate decreased sharply when the pressure was increased at 425°C and Mo(CO)₆ flow rate of 4.5 mg/min (Figure 7).

The films deposited at 425 °C decreased in thickness across the wafer in the direction of flow. At the leading edge of the MoO₃ deposits the films were 12.5 kÅ thick and decreased in thickness to 1 kÅ at the trailing edge. For a film deposited at 270 mtorr, the film was 16.0 kÅ thick at the leading edge and decreased to 4 kÅ at the opposite edge.

Water vapor was also added to the gas stream to reduce the carbon content of the films. However, there was no quantifiable difference in film composition or morphology when the water flow rate was varied from 0.0 to 0.51 sccm.

3.2 Process Variables at 5 sccm O₂

Films were deposited at an oxygen flow rate of 5 sccm while varying the pressure (200-500 mtorr) and temperature (425-500°C). The levels at which the pressure and temper-
Figure 6 Schematic of mixed molybdenum oxide film deposited at 425°C and 370 mtorr

Figure 7 Molybdenum oxide deposition rate versus pressure at temperature of 425°C with a Mo(CO)$_6$ flow rate of 4.5 mg/min with an oxygen flow rate of 15 sccm
Table III  Experimental settings and deposition results for O\textsubscript{2} flow rate of 5 sccm

<table>
<thead>
<tr>
<th>Run</th>
<th>Seq.</th>
<th>Press (mtorr)</th>
<th>Temp (°C)</th>
<th>Deposit (% α-MoO\textsubscript{3})</th>
<th>CO/CO\textsubscript{2} (A/A)</th>
<th>Dep. rate (mg/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>200</td>
<td>425</td>
<td>0</td>
<td>64.8</td>
<td>0.180</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>200</td>
<td>475</td>
<td>2</td>
<td>58.7</td>
<td>0.180</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>200</td>
<td>475</td>
<td>3</td>
<td>60.5</td>
<td>0.187</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>400</td>
<td>425</td>
<td>39</td>
<td>41.9</td>
<td>0.137</td>
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<tr>
<td>4</td>
<td>4</td>
<td>400</td>
<td>475</td>
<td>100</td>
<td>35.1</td>
<td>0.133</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>300</td>
<td>450</td>
<td>25</td>
<td>44.9</td>
<td>0.153</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>300</td>
<td>450</td>
<td>8</td>
<td>44.0</td>
<td>0.167</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>300</td>
<td>450</td>
<td>10</td>
<td>45.3</td>
<td>0.160</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>300</td>
<td>500</td>
<td>100</td>
<td>40.1</td>
<td>0.187</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>500</td>
<td>450</td>
<td>100</td>
<td>29.1</td>
<td>0.123</td>
</tr>
</tbody>
</table>

The same general trends on the deposits formation at the high gas flow rate were observed at 5 sccm. The films were characterized using Raman, FTIR, XRD and XPS. The α-MoO\textsubscript{3} films were formed at temperatures between 450-500°C (Table III and Figure 8). The α-MoO\textsubscript{3} films were polycrystalline with preferred (0k0) orientation. XRD and Raman characterization revealed nearly identical spectra to those in Figures 2 and 3. The morphology of the light gray α-MoO\textsubscript{3} deposits showed a columnar structure. At lower temperatures bluish-black reduced oxides were produced.
The deposition pressure had a pronounced influence on the composition, deposition rate, uniformity and gas phase composition. α-MoO$_3$ films were deposited at pressures > 300 mtorr while reduced oxides were favored at lower pressures (Table III and Figure 8). Gradations in film thickness were also observed in the direction of flow (Figure 9). The film thickness was influenced by the parameters as well as the physical geometry of the reactor. Increasing the pressure from 200 to 400 mtorr at 475°C produced a steeper gradation in film thickness (Figure 9). It appeared that both the temperature and pressure were synergistically coupling to influence the composition which was determined by modelling the response.

A model of α-MoO$_3$ formation as a function of temperature and pressure was developed. The model consisted of 5 terms including both linear and quadratic expressions.
\[ Y_{\text{MoO}_3} = 19.9 + 36.5X_p + 15.3X_T + 13.6X_pX_T + 13.2X_T^2 \]  

(4)

All five terms are statistically significant at a 95% confidence interval\(^\text{18}\).

The model fit of the data is expressed in two ways. The \(R^2\) for the model is 0.977 (Table IV); this value indicates that 97.7% of the variability in the data is accounted for in the model. A model with a perfect fit would have an \(R^2\) of 1.0. The F-value for the model is 53.8 which gives an indication of the explanatory force of the model (Table IV). A model that did not have any explanatory force at a 95% confidence interval would have an \(F_{(4,5)}\) value less than 5.19\(^\text{18}\).

Figure 9 Film thickness measurements for two films deposited with an oxygen flow rate of 5 sccm
Table IV  Analysis of variance for regression model for 5 sccm O₂ flow rate

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of Freedom</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>4</td>
<td>16952.3</td>
<td>4238.0</td>
<td>53.8</td>
</tr>
<tr>
<td>Error</td>
<td>5</td>
<td>393.8</td>
<td>78.8</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>9</td>
<td>17346.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( R^2 = 0.977 \)

| Variable | Coefficient | Std. Error | T-Value | P > |T| |
|----------|-------------|------------|---------|-----|---|
| Intercept| 19.9        | 3.73       | 5.35    | 0.0031 |
| \( X_p \) | 36.6        | 3.07       | 11.91   | 0.0002 |
| \( X_r \) | 15.3        | 3.99       | 3.82    | 0.0123 |
| \( X_pX_r \) | 13.6        | 4.10       | 3.31    | 0.0212 |
| \( X_r^2 \) | 13.2        | 3.17       | 4.16    | 0.0088 |

Pearson correlation coefficients were evaluated for all the variables. Coefficients were calculated for pressure deposition rate (-0.911), pressure [CO/CO₂] (-0.927) and pressure α-MoO₃ (0.756) and indicate that the pressure is an influential process variable on all three responses. The negative values indicate that as pressure increases these values decrease.

The predicted values from the model using equation (4) and experimental values were compared (Table V). The residual was determined by subtracting the predicted value from the actual response; the values of the residuals varied from 7 to -12 with the predicted values ranging from -1.7 to 103.3 (Table V).
Table V MoO$_3$ film predicted and experimental values for O$_2$ flow rate of 5 sccm

<table>
<thead>
<tr>
<th>Run</th>
<th>Sequence</th>
<th>α-MoO$_3$</th>
<th>Predicted</th>
<th>Residual</th>
</tr>
</thead>
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<tr>
<td>2</td>
<td>3</td>
<td>2</td>
<td>-1.7</td>
<td>3.7</td>
</tr>
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<td>3</td>
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<td>5</td>
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<td>6</td>
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<td>100</td>
<td>103.3</td>
<td>-3.3</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>100</td>
<td>93.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>
4 DISCUSSION

This section contains material on both CVD fundamentals such as thermodynamics and transport phenomena as well as analysis of actual experimental results. Thermodynamic equilibrium calculations are presented in section 4.1. The experimental design results and model are discussed in section 4.2. The overall influence of pressure, temperature, and transport processes on the depositions are discussed in sections 4.3 and 4.4.

4.1 Thermodynamics

To determine the most stable phase of molybdenum oxide that would deposit in the Mo(CO)$_6$, O$_2$ and H$_2$O thermal deposition process, a computer program, Solgasmix-PV$^{10}$, was used to calculate the equilibrium composition. The program can be used to calculate equilibrium compositions for gases, solids and mixtures. The program calculated the gas phase and solid composition by minimizing the summation of the free energies of all the species. The method minimizes the total Gibbs free energy of the system by solving a series of equations using Lagrange's method of undetermined multipliers and Taylor expansions around the moles of each species.

Equilibria were calculated for both a three component Mo, O, and C system consisting of 14 gas species and 9 solid compounds plus a four component Mo, O, C, and H system consisting of 56 gas species and 9 solid compounds. For both three and four component systems the solid species consisted of C(graphite), Mo, Mo$_2$C, Mo(CO)$_6$, MoO$_2$, Mo$_3$O$_{11}$,
Mo\textsubscript{3}O\textsubscript{24}, Mo\textsubscript{5}O_{25}, and \(\alpha\)-MoO\textsubscript{3}. The data was entered into the program using an input file containing the deposition conditions at constant T, P and moles of each species. The thermodynamic data used in the calculations was taken from the JANAF tables\textsuperscript{20,21}.

Equilibria were calculated over a range of temperatures 127-527\degree C, pressures 100 - 1000 mtorr and gas compositions. The \(O_2/\text{Mo}(\text{CO})_6\) molar ratio was varied from 1 - 200 and \(\text{H}_2\text{O}/\text{Mo}(\text{CO})_6\) molar ratio was varied from 0 - 3. Based upon equilibrium calculations for the above conditions, \(\alpha\)-MoO\textsubscript{3} is the only solid component formed as long as the \(O_2/\text{Mo}(\text{CO})_6\) ratio was 5 or greater. When \(O_2\) was in excess, the gas phase consisted primarily of \(\text{CO}_2\) and \(O_2\). Varying the water vapor composition in the gas phase had little effect on the equilibrium.

Calculating the thermodynamic equilibria under various conditions provided insight into the Mo-O deposition. As noted by the thermodynamic calculations, MoO\textsubscript{3}, in the presence of excess oxygen, is the most stable phase from 127-525\degree C, but was deposited only at temperatures of 425-500\degree C depending upon the system pressure. The conditions under which \(\alpha\)-MoO\textsubscript{3} is formed is at temperatures \(\geq 425\degree C\) with pressure > 600 mtorr with an \(O_2\) flow rate of 15 sccm and at pressures > 300 mtorr and temperature > 450\degree C with \(O_2\) at 5 sccm.

Equilibria calculations show that the gas phase consists of primarily \(\text{CO}_2\) and \(O_2\). During actual depositions mass spectrometry indicates that the gas phase contains primarily \(\text{CO}, O_2\) and \(\text{CO}_2\) in decreasing order of concentration. The ratio of \(\text{CO}-\text{CO}_2\) in the gas phase varied with the film composition (Table III); the \(\text{CO}/\text{CO}_2\) signal ratio was the lowest (29.1-40.1) and thus \(\text{CO}_2\) concentration highest when MoO\textsubscript{3} was deposited. Accordingly, analysis of both the gas and solid phase indicate the process was not limited by thermodynamics but
by the reaction kinetics. This is in agreement with most CVD processes which are controlled by the reaction kinetics\textsuperscript{22}.

4.2 Statistical Model

Modeling LPCVD systems is difficult due to the process complexity. From the results in Table II and III a quadratic model was developed that consisted of four terms plus an intercept (Equation 4). The significance of each term is indicated by the magnitude of the t-values and coefficients since the standard errors are similar (Table IV). A regression analysis indicated that all four terms: temperature, pressure, temperature*pressure and temperature*temperature contribute to the formation of oriented $\alpha$-MoO\textsubscript{3} films. A generalized two dimensional plot was constructed that depicts the effect of temperature and pressure on the formation of $\alpha$-MoO\textsubscript{3} (Figure 8). The plot also gives a clear indication that temperature and pressure are interacting by the fact that $\alpha$-MoO\textsubscript{3} is formed by increasing either temperature or pressure at the center point.

Three terms in the model are temperature related which is understandable considering the process is thermally activated and the deposition temperature regulates the reaction kinetics. The model indicates that pressure is the single most influential parameter on the depositions according to t-statistics (Table IV). As will be noted, varying the system pressure regulates the residence time, gas velocity, gas phase temperature profiles\textsuperscript{22} and film composition. The mechanistic relationship between film deposition and the process variables is not fully understood, but it does appear that the system pressure and temperature synergistically influence the deposition.
Modeling the response of the central composite design used for 5 sccm depositions gives an indication whether the response is linear or quadratic as a function of the process variables. Comparisons of the α-MoO$_3$ content of the depositions with the predicted values for the model in some cases underestimate (< 0) the response at low levels and overestimate (> 100) the response at high levels (Table V). Since the minimum response is 0 and the maximum response is 100, it appears that a cubic expression may provide a better fit of the data. However, since the temperature and pressure range was small a quadratic expression adequately fits the data. Researchers have found that the pyrolysis of various precursors, based on percentage, versus temperature has a cubic response.

4.3 Process Variable Effects

4.3.1 Deposition temperature

As noted in Figure 5, the deposition rate decreased with increasing temperature for an O$_2$ 15 sccm flow rate. Mo(CO)$_6$ begins to decompose at 150°C and is completely decomposed by 450°C in an evacuated chamber. In the present study the material deposited uniformly on the substrate at 300°C, but at 350°C some of the material deposited on the walls of the chamber surrounding the susceptor. This trend increased as the temperature of the substrate was raised which explains why the deposition rate decreases with temperature (Figure 5). This phenomenon, homogeneous gas phase nucleation, is due to the high thermal gradients surrounding the susceptor which cause the precursor to decompose before it reaches the susceptor resulting in wall deposits and is frequently encountered with metalorganic precursors at high substrate temperatures.
Films depositing on the substrate varied in thickness across the surface at the high temperatures (Figure 9 and page 35). This is due to a decrease in the precursor concentration in the axial direction resulting from deposits on the chamber wall and fast reaction rate on or near the substrate surface. It has been reported in the literature that in order to form uniform deposits in a cold wall reactor, at least 50% of the precursor should bypass the substrate without reaction. In the present case, the Mo(CO)$_6$ content in the gas phase was too low to measure with mass spectrometry when $\alpha$-MoO$_3$ films were deposited.

Although substrate temperatures in excess of 425°C resulted in non-uniform films and low deposition rates, it was necessary to deposit at high temperatures in order to deposit $\alpha$-MoO$_3$ films. The high temperatures were required because the process is thermally activated. Therefore, there is a trade-off between substrate temperature, material composition, film uniformity and gas phase nucleation. This may explain why other researchers deposited uniform MoO$_3$ films at 300°C and then oxidized the deposits in a separate step at 500 or 600°C to produce $\alpha$-MoO$_3$.

The affect of the temperature on the deposition rate is frequently classified into three regimes$^{21,23,25,26}$: kinetically controlled, mass transfer controlled and gas phase decomposition (page 9). A kinetically controlled process shows the deposition rate increases as temperature increases. The mass transfer region depicts the deposition rate as independent of temperature because all of the material reaching the substrate is reacting and the deposition rate is limited by the diffusion of the precursor to the substrate surface. The gas phase decomposition region is characterized by the precursor partially decomposing in the gas phase and depositing on both the walls and substrate. Using this classification scheme MoO$_3$ films are depositing...
in the gas phase decomposition region for both flow rates at high temperatures. Lander and Germer\textsuperscript{12} reported that the difficulties encountered at high temperatures from Mo(CO)\textsubscript{6} decomposition can be reduced by decreasing the system pressure.

4.3.2 Deposition pressure

Pressure strongly influenced the deposition rate and composition (Figures 7 and 8). Examining the underlying principles that are a function of pressure such as residence time and transport processes can explain the deposition results.

The system pressure was regulated by throttling a bellow valve located on the roughing pump intake line. For the depositions, two gas flow rates, 5 and 15 scm/min were used which corresponded to a base pressure of 71 and 150 mtorr respectively with the valve fully open. To obtain a higher pressure the valve was adjusted manually. For both flow rates increasing the pressure increased the residence time of the reactants and decreased the gas velocity.

The residence time, \( \tau \), of the gas was calculated using the equation

\[
\tau = \frac{PV}{Q} \tag{5}
\]

where \( P \)-chamber pressure, \( V \)-volume and \( Q \)-flow rate. The volume, 1030 cm\textsuperscript{3}, was equated to the chamber volume surrounding the susceptor \( \pi R^2 L \), where \( L \) is the length shown in Figure 1, minus the susceptor volume \( \pi t \), where \( t \) is the susceptor thickness. From equation 5, the residence time was proportional to pressure, \( \tau \sim P \). For the deposition at 15 sccm the range of pressures used during the depositions was 265-1014 mtorr which corresponded to residence times from 1.4 to 5.5 s. At a flow rate of 5 sccm, the residence times were 3.2 -
8.0 s. The residence time required for homogenous α-MoO$_3$ films to form at 15 sccm was 3.6-5.5 s and 4.9-8.0 s for an O$_2$ flow rate of 5 sccm.

As stated before, gas phase decomposition can be reduced at high temperatures by decreasing the system pressure. This appears to be true but decreasing the system pressure on a flow through reactor has wider implication on the deposits as will be discussed in the following section.

4.4 Transport Phenomena

Transport phenomena in CVD reactors have been studied using both experimental and computational techniques. Both methods indicate that the gas flow patterns control the deposition rate uniformity and composition. This is because the gas streamlines are influenced by the heat transferred from the susceptor, by radiation, convection and conduction, to the gas and reactor walls. Therefore, thermal gradients exist in the gas phase which are a function of the gas velocity and substrate temperature (Figure 10). At high gas velocities an unheated region of gas called a cold finger extends over the substrate (Figure 10). The cold finger contains reactant that will decompose further downstream resulting in a uniform deposition. At low velocities the isotherms extend further into the gas causing gas phase reaction, reactant depletion and uneven coatings (Figure 7 and 9).

For the Mo-O depositions both the film uniformity and composition can be explained in terms of transport phenomena and reaction kinetics. Since the gas flow rate was fixed varying the pressure resulted in a corresponding change in the residence time and gas velocity. The residence time is inversely proportional to the gas velocity in this system. The
Figure 10 Comparison of measured (dashed lines) and predicted (solid lines) gas temperatures above a susceptor in a horizontal reactor for two inlet flow velocities of $\text{H}_2$ (a) 2 standard liters per minute (slm) (b) hydrogen at 8 slm. Note: the y-axis indicates distance (mm) above the substrate and in case (b) the cold finger is observed.
atmospheric CVD studies of molybdenum oxides pointed out that MoO₂ deposits readily from Mo(CO)₆ at 300°C⁸. But, to form α-MoO₃ sufficient time and energy are needed for the Mo species to become fully oxidized and for adatom surface diffusion to form crystalline deposits. For LPCVD, at low pressures (high gas velocities and low residence time) the deposited films were more uniform due to less gas phase heating or the cold finger effect²⁷. At these pressures (< 600 mtorr at 15 sccm and < 300 mtorr at 5 sccm) material was depositing on the surface faster than it could be fully oxidized and for adatom surface diffusion to an appropriate crystalline kink site²³,²⁷. At higher pressures (low velocities and high residence time) isotherms extend into the gas phase which decompose the precursor resulting in MoO₃ films of uneven thickness (page 35 and Figure 9). Eversteyn²² reported for a horizontal CVD reactor, Si film uniformity was the highest at high gas velocities.

It appears that it is the precursor gas phase reactions in addition to the rate at which the material arrives at the substrate and reacts with oxygen that determines the composition of the film. The influence of deposition rate and precursor flow rate on the α-MoO₃ content of the film was examined by depositing films at 425°C and 470 mtorr where both phases coexisted on the substrate at an O₂ flow rate of 15 sccm. Increasing the precursor flow rate from 2.3 to 4.5 mg/min decreased the MoO₃ content of the film from 85 to 50% Therefore, controlling the pressure and precursor flow rate regulated the rate at which precursor arrives at the substrate surface. And it is the transport processes in addition to temperature which determine the oxidation kinetics and ultimately the deposit composition. Similar results were observed in a molybdenum oxide reactive sputtering system where the deposition rate controlled the structure of the deposits and molybdenum oxygen stoichiometry⁹,¹⁰.
5 CONCLUSIONS

The feasibility of producing molybdenum trioxide films was demonstrated using a LPCVD system with oxygen gas flow rates of 5 and 15 sccm. Thermodynamic equilibrium calculations of the system showed that α-MoO₃ is the most stable phase and would form over a wide range of temperature and pressure. Actual depositions showed that the material would deposit over a narrow range of conditions and its formation was influenced by temperature, pressure and Mo(CO)₆ flow rate. The deposition composition and uniformity were controlled by transport phenomena and reaction kinetics. The thickness of the films were more uniform at lower pressures, however, it was not possible to produce homogeneous MoO₃ films at low pressures. The precursor, Mo(CO)₆, had a high vapor pressure at room temperature, but it rapidly decomposed in the gas phase near the substrate forming reduced molybdenum oxides at 350°C. However, MoO₃ films were formed at higher temperatures, 425°C, and high pressures at low Mo(CO)₆ flow rates. The significance of temperature and pressure on the depositions with an oxygen flow rate of 5 sccm was determined using a quadratic model. The model indicated that temperature and pressure act synergistically on the deposits. Films deposited at an oxygen flow rate of 5 sccm at pressures between 300-500 mtorr required a slightly higher substrate temperature (25-50°C) in order to produce MoO₃ films compared to the 15 sccm results due to pressure-temperature interaction. The presence of water in the gas stream had little effect on the film composition.
REFERENCES


APPENDIX A REDUCED MOLYBDENUM OXIDES

Results at 15 sccm O₂

The influence of temperature on films deposited at an oxygen flow rate of 15 sccm was determined by characterization with XRD and Raman spectroscopy (Figure A1 and A2). Raman spectroscopy and XRD revealed that films deposited at lower temperatures consisted of MoO₂, Mo₂O₁₁, and Mo₅O₁₄ with MoO₃ forming at the highest temperature. As noted from the spectra, the oxygen content of the films increased with temperature. The Mo₅O₁₄ material is the most difficult to characterize because it does not have a Raman spectrum and has only been synthesized as a bulk powder in the literature¹. Several of the films resembling Mo₅O₁₄ were removed from the substrate and ground to produce a powder to compare with reported XRD patterns (Table A1). XRD comparisons were made between a Mo₅O₁₄ powder¹ and a ternary material³³ V₀.₀⁹Mo₀.₉₁O₁₄ which has a similar structure to Mo₅O₁₄. The most intense peaks from the ground films match those of Mo₅O₁₄ and Si powder diffraction patterns from the JCPDS data base. However, neither of the patterns from the literature gives diffractions below 2.2Å.

XPS characterization of this material showed a spectrum similar to α-MoO₃ but the peaks were much broader. An XPS comparison between the film and Mo₅O₂₉₋₁ materials produced by McCormick were in good agreement²⁴. In XPS the broadening of the peaks is caused by differences in the coordination environment of the molybdenum atoms. Auger and XPS of the Mo₅O₁₄ deposits contained no impurities other than a small amount of carbon (<
Table AI XRD powder comparison of film and powders

<table>
<thead>
<tr>
<th>Ground Films</th>
<th>JCPDS powder patterns*</th>
<th>(V_{0.07}Mo_{0.93})<em>{2}O</em>{14}b</th>
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<td>D (Å)</td>
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<td>D (Å)</td>
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<tr>
<td>1.64</td>
<td>Si</td>
<td>1.64</td>
</tr>
</tbody>
</table>

a-JCPDS Mo_{2}O_{14} powder pattern contains diffractions from 11.5-2.85 Å
b-powder pattern contains diffractions from 11.4-2.21 Å

1%). Auger and XPS of the MoO_{2} and Mo_{4}O_{11} materials were not completed but previous researchers reported molybdenum oxide films produced at 300°C contained approximately 1% carbon. All the reduced oxides deposits could be transformed into α-MoO_{3} deposits by heating at 500°C under ambient environment.

The influence of pressure on the deposits at 425°C is shown in Figure 3A. These films were polycrystalline and consisted of mixtures of reduced molybdenum oxides from pressures of 217 - 370 mtorr. At 470 mtorr, the film consists of Mo_{2}O_{14} and α-MoO_{3}. The reduced oxides were easy to identify because of their bluish-black color compared to α-MoO_{3} which is off-white or light gray. Several of the films also show a Si (200) diffraction at 2.72Å (Figure 3A).
Figure 1A  Raman spectra of films deposited at a pressure of 670 mtorr and temperature of (a) 300°C [MoO₂] (b) 350°C [Mo₄O₁₁] (c) 375°C [Mo₉O₄₆] (d) 425°C [α MoO₃]
Figure 2A  XRD patterns of films deposited at a pressure of 670 mtorr and temperature of (a) 300°C [MoO₂] (b) 350°C [Mo₂O₇] (c) 375°C [Mo₅O₁₁] (d) 425°C [α MoO₃]
Figure A3  XRD pattern of films deposited at a Mo(CO)$_6$ flow rate of 4.5 mg/min, 425°C and pressures of (a) 217 mtorr (b) 270 mtorr (c) 370 mtorr and (d) 470 mtorr
Results at 5 sccm O₂

Before beginning the depositions with a 5 sccm flow rate of oxygen, films were deposited over a range of temperatures, pressures, and Mo(CO)₅ flow rates (Table AII). The films were primarily deposited on the SiC coated graphite susceptor and were analyzed based upon film color and Raman spectroscopy. The most interesting aspect about these deposits was that even at the lowest Mo(CO)₅ flow rate at 530°C and lowest pressure (resulting in high gas velocities) the film was not entirely α-MoO₃.

<table>
<thead>
<tr>
<th>Run</th>
<th>Q₁₀₀(CO) (mg/min)</th>
<th>Pressure (mtorr)</th>
<th>Temperature (°C)</th>
<th>Deposit* (% α-MoO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>10</td>
<td>1.44</td>
<td>500</td>
<td>450</td>
<td>100</td>
</tr>
</tbody>
</table>

* - films were deposited on the susceptor with analysis based upon film color and Raman spectroscopy
PAPER 2

LOW PRESSURE AND INDUCTIVELY COUPLED PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF $\alpha$-MoO$_3$ FROM Mo(CO)$_6$ AND O$_2$

USING EXPERIMENTAL DESIGN
ABSTRACT

Thin films of α-MoO₃ were produced from Mo(CO)₆ and O₂ using both PECVD and LPCVD. Statistical experimental design was used to develop a parametric model for the deposition of oriented (0k0) films on silicon substrates. A linear model was developed by regulating four variables: temperature, pressure, RF current and Mo(CO)₆ flow rate. All the variables plus four interaction terms were found to influence the film composition and orientation. A linear model was used to describe the data although the data appear to fit a cubic model.

Comparing LPCVD and PECVD techniques under the same conditions indicated that crystalline α-MoO₃ films were produced at 75-100°C lower in the presence of a plasma. It was demonstrated that a low frequency (200-450 kHz) RF generator could be used to create an Ar-O₂ plasma for the deposition. The plasma formation was influenced by the RF current and the concentration of Mo(CO)₆ in the gas phase. The deposition rate of PECVD films was approximately 75% lower than LPCVD films. The formation of α-MoO₃ films and the deposition rate were negatively correlated.
1 INTRODUCTION

In recent years there has been considerable interest in using low-pressure glow discharges for promoting chemical reactions to produce films of materials that are difficult or perhaps impossible to produce by conventional techniques\(^1\). This has resulted in the development of novel processes and materials such as diamond films and amorphous hydrogenated silicon films. One such plasma process, plasma enhanced chemical vapor deposition, PECVD, is a vapor technique where a material is produced from a reacting gas flowing into a gas discharge, ultimately depositing a solid phase on a substrate. The discharge is created by excitation of the gas phase by a radio-frequency (RF) or microwave field. The presence of the plasma in the deposition process acts as a catalyst to reduce the energy of activation for the film forming reaction.

Recently, interest in plasma enhanced chemical vapor deposition (PECVD) has increased due to lower substrate temperature requirements for microelectronic devices. Most of the published research using PECVD has focused on producing materials used in the electronics industry. Little fundamental research has been reported on using PECVD to produce other materials including refractory metal oxides.

Thin films of molybdenum oxide are of interest due to specific applications. Treated amorphous $\alpha$-MoO$_3$ films have recently achieved attention because of photochromic and electrochromic properties which have potential uses in display devices\(^2\). MoO$_3$ films have also been used as resists for semiconductor processing\(^3\). Crystalline MoO$_3$ with preferred orientations has been studied extensively because of its catalytic activity\(^4\).
The synthesis of α-MoO₃ films has been accomplished using sputtering, CVD, evaporation, and exfoliation. Reactive sputtering can produce molybdenum oxides of different stoichiometries by controlling the target power. CVD researchers have found that deposition temperature influence the deposits composition. Little has been reported on using PECVD to produce MoO₃ besides a feasibility study to produce amorphous molybdenum oxide films for electrochromic application tests. In the latter study, the plasma was generated using a capacitively coupled 13.56 MHz RF generator and little attention was paid to material composition or to the influence of process parameters on the deposition.

The above studies have focused on producing films by traditional methods by varying one factor at a time (OFAT). This type of experimentation does not account for synergistic effects between process variables, and the conclusions drawn from this approach are localized. CVD processes are very complex with the process being influenced by thermodynamics, reaction kinetics, mass transport and film growth mechanisms. Since it is the process parameters that are controlling the film formation, it is important to consider how each of these and their interactions influence the deposited material.

Statistical experimental design consists of choosing the experimental conditions and analyzing the results in order to formulate an empirical model. The response or output variable, upon which the model is based, is a function of the process input variables that affect it. Utilizing this technique it is possible to minimize the number of experiments and to determine which variables or interactions of variables are truly influencing the response.

This method has become popular in the semiconductor industry in the past 10 years for both etching and depositing films. To use this technique a matrix is constructed
consisting of the process variables and the levels under with the experiments will take place. Several researchers\textsuperscript{14,15} used this technique to produce SiNH and Si\textsubscript{3}N\textsubscript{4} films using LPCVD and PECVD. The PECVD SiNH films were strongly influenced by RF power and gas composition\textsuperscript{14}. The LPCVD Si\textsubscript{3}N\textsubscript{4} responses had significant interactions between temperature, deposition time, and gas flows\textsuperscript{15}.

The present study was undertaken to compare the use of LPCVD and PECVD to produce crystalline $\alpha$-MoO\textsubscript{3} films with (000) orientations. The importance of the four process variables (temperature, pressure, RF current, and Mo(CO)\textsubscript{6} flow rate) and interactions on the orientation of the films was quantified using statistical experimental design. In this study an inductively coupled RF generator of 200-450 kHz was used to generate an Ar-O\textsubscript{2} plasma, this frequency has not been used to produce plasma deposited MoO\textsubscript{3} films.
2. EXPERIMENTAL PROCEDURE AND CHARACTERIZATION

The films were prepared using a chamber as depicted in Figure 1. The quartz cylindrical chamber was surrounded by an induction coil which was connected to a 5 kW Lepel, 200 - 450 kHz, RF generator. The generator was used to create a glow discharge with the sample heated by a custom designed Macor resistive heater. The temperature of the heater was measured with a K-type thermocouple connected to a Eurotherm 818P programmable temperature controller. Feed mixtures of Ar (99.995 %, Matheson), O₂ (99.97 %, Matheson), and Mo(CO)₆ (99 %, Alfa) were used. The O₂ to Mo(CO)₆ molar ratio in the gas stream was regulated by varying the quantity of gas flowing through a Mo(CO)₆ sublimator maintained

![Figure 1 PECVD and LPCVD chamber for molybdenum oxides](image-url)
at 30°C. The concentration of Mo(CO)$_6$ in the gas phase was determined by collecting the vaporized precursor in a cold trap after the sublimator and correlating the mass of the sublimed Mo(CO)$_6$ with gas flow rate. Brooks mass flow controllers were used to regulate the flow rate of oxygen and argon. The pressure in the system was measured with an MKS capacitance manometer and regulated by throttling a bellow valve located in the roughing pump intake line. A UTI 100C mass spectrometer with an ISS-325 sampling system were used to analyze the effluent.

Prior to film depositions, the sample was heated to 450°C; evacuation by a turbomolecular pump produced a pressure of 1 x 10$^{-7}$ torr. A 2" silicon (100) wafer was used as the substrate; no attempt was made to remove surface oxide. The RF generator current was adjusted to achieve the desired setting on a Simpsons 50 RF amp meter. The carrier gas was then admitted into the chamber for one hour prior to the deposition. After the desired deposition time (30 minutes), Ar was used to purge the chamber while the sample/heater was allowed to cool to room temperature.

The deposited films were characterized with a Nicolet 60SX Fourier transform infrared spectrometer, Spex Triplemate laser Raman spectrometer, PHI 5300 ESCA system, Scintag X-ray diffractometer (XRD), a JEOL scanning electron microscope (SEM), and a Tencor alpha step profilometer.
3 METHODOLOGY

A central composite design was chosen to determine the relative importance of the four factors (temperature, pressure, Mo(CO)$_6$ flow rate, and RF current) on the deposition rate and the film orientation. Three other variables were held constant including deposition time, O$_2$ and Ar flow rates (Table I).

Depositions were conducted at two levels of each variable, $2^4$, giving a total of 16 depositions plus four depositions at intermediate values of the parameters to check for curvature$^{16}$ (Table I). The depositions were run in a randomized order as indicated by the sequence number. After the initial 20 depositions, eight more were completed: four replicates plus four depositions conducted at the axial points.

Table I Deposition conditions used for experimental design

<table>
<thead>
<tr>
<th>Process Variables</th>
<th>Levels</th>
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<td>Pressure (mTorr)</td>
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</tr>
<tr>
<td>Temperature (°C)</td>
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</tr>
<tr>
<td>RF current (amps)</td>
<td>(22, 26°F, 30, 34°F)</td>
</tr>
<tr>
<td>Mo(CO)$_6$ flow rate (mg/min)</td>
<td>(0.56°F, 1.00, 1.44°F, 1.88)</td>
</tr>
<tr>
<td>Ar flow rate (sccm)</td>
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</tr>
<tr>
<td>O$_2$ flow rate (sccm)</td>
<td>5</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>30</td>
</tr>
</tbody>
</table>

ap - axial point           sccm - standard cm$^3$/min
cp - center point


Two process responses were tabulated; they included the ratio of (0k0) orientation of the $\alpha$-MoO$_3$ in the deposit and the deposition rate. The degree of crystalline orientation of $\alpha$-MoO$_3$ in the deposits was quantified using this expression:

$$R_{(0k0)}^{\alpha} = \frac{I_{3.46}}{I_{3.46} + I_{3.81} + I_d} \times 100\% \quad (1)$$

where $R_{(0k0)}^{\alpha}$ is the XRD peak intensity percentage of (0k0) $\alpha$-MoO$_3$ in the deposit, $I_{3.46}$ is the $\alpha$-MoO$_3$ (040) peak at 3.46Å, $I_{3.81}$ is the $\alpha$-MoO$_3$ (110) peak at 3.81Å, and $I_d$ is the XRD peak intensity of any peak not attributed to $\alpha$-MoO$_3$. The deposition rate was determined by weighing the Si wafer before and after the deposition and then dividing the difference by the deposition time.

The results of the design were analyzed using a least squares regression analysis. In the analysis, the process variables were standardized according to the following formulas:

$$X_{QHD} = \frac{(Q_{\text{HD}} - 280)}{280} \quad (2)$$

$$X_F = \frac{(\text{PRESS} - 280)}{280} \quad (3)$$

$$X_T = \frac{(\text{TEMP} - 350^\circ)}{350^\circ} \quad (4)$$

$$X_{RF} = \frac{(RF \text{ AMPS} - 26)}{26} \quad (5)$$

Only the variables that were significant at a 95% confidence interval were included in the analysis.
4 RESULTS

4.1 Characterization

X-ray diffraction was used to analyze the crystal structure of the deposits and to classify the α-MoO₃ response as in Eq. (1). Four types of patterns were observed from the deposits (Figure 2). The first two patterns (Figure 2a and 2b) indicated that α-MoO₃ was the only crystalline material present as noted by the diffractions at 6.93, 3.81, 3.26 and 2.31 Å which corresponded to the (020), (110), (040) and (060) planes of α-MoO₃.¹⁸ The difference in the two patterns was due to the degree of (0k0) orientation in the films. Two other types of patterns were observed, one a mixed deposit consisting α-MoO₃ and a reduced molybdenum oxide and the other was a reduced molybdenum oxide (Figure 2c and 2d).

The vibrational spectrum of the same four deposits was also recorded (Figure 3). Bands at 584, 872, and 995 cm⁻¹ indicated that α-MoO₃ is the only molybdenum oxide present (Figure 3a and 3b).¹⁹ For the other two films the number of bands increases for the mixed phase film (Figure 3c) and the bands broaden for the reduced molybdenum oxide (Figure 3d).

The chemical composition of the films was determined by XPS. The surface of six films were characterized using XPS, and depth profiling was completed on two films. The electron binding energies of the Mo 3d₅/₂ and 3d₃/₂ for the α-MoO₃ films were in good agreement with literature values.²⁰ The surface of the films contained absorbed carbon but
Figure 2  XRD patterns of films deposited under PECVD conditions
Figure 3  FTIR spectra of films deposited under PECVD conditions with $R_{\text{film}}$ values listed in Table II (a) run 13 [100] and (b) run 9 [88] and LPCVD conditions (c) run 7 [84] and (d) run 19 [0] (the run numbers are listed in Table II)
depth profiling of two of the films indicated that within the bulk of the film the carbon content < 1 % (Figure 4).

SEM micrographs revealed the differences in morphology of the PECVD deposits at two different temperatures (Figure 5). A film deposited at 312°C (run 11) had a columnar structure (Figure 5a) whereas a film deposited at 387°C (run 15) had a platelet type structure (Figure 5b).

Film thickness was measured using a profilometer for several PECVD and LPCVD films. The PECVD films were relatively uniform in thickness from 0.22-0.4 μm for runs 11...
Figure 5  SEM micrographs of PECVD films deposited at a) 312.5°C [run 9, S-30] and b) 387.5°C [run 15, S-5]
Figure 6  Mass spectrum for the first 15 minutes of deposition for run 13. The background readings are from 0-2.4 min and deposition from 2.4-15 min. The signals in the scan correspond to mass to charge ratios of 28, 32, and 44.

and 13. Film deposited under LPCVD conditions were thicker with thickness ranging from 1.0-1.5 um for runs 23 and 24.

The gas phase was also analyzed during the depositions using a mass spectrometer. The effluent consisted of primarily 4 species CO(28), CO₂(44), Ar(40), and O₂(32) as indicated by their mass charge ratio (Figure 6). For all runs O₂ was present in excess (Figure 6) and the composition of the gas phase did not change during the course of the deposition (Figure 6). The major difference in the gas composition between depositions was the CO/CO₂ ratio. For depositions in which a plasma was observed with a Mo(CO)₆ flow rate
of 1.00 mg/min, the CO/CO₂ ratio averaged 10 whereas the ratio was approximately 40 when a plasma was not present.

4.2 Experimental Design

Each of the four process variables directly influenced the relative intensity of the (0k0) orientation of α-MoO₃ in the deposits (Table II). The most influential variable was the RF current particularly at high values. At RF values of 30 amps and Mo(CO)₆ flow rate of 1.00 mg/min, a plasma formed in the chamber. The plasma appeared as a diffuse white discharge surrounding the substrate (Figure 7a). The plasma led to an increased response, that was not observed when the RF current was 22 (Tables II and III, Figure 7b).

The precursor flow rate appears to interact with the RF current and to inhibit the plasma formation at 1.88 mg/min. In one instance, run 16, a plasma was observed with a Mo(CO)₆ flow rate at 1.88 mg/min with the RF at 30 and pressure of 350 mtorr but the plasma was unstable.

The deposition temperature had two effects on the deposits. First, it increased the response as noted when comparing runs 3 and 4 with 7 and 8 (Table II). Secondly, it increased the crystallinity of the deposits. That is, the XRD peak intensity was higher for the films deposited at 387.5°C compared to 312.5°C.

Of the four variables the pressure had the least influence on the depositions (Tables II and III). But overall, increased pressure increased the response as observed when comparing the depositions at pressures of 210 and 350 mtorr.
Figure 7  Photographs of chamber during depositions with the room lights turned off for (a) PECVD and (b) LPCVD processes
Table II  Experimental results for composite design with center points

<table>
<thead>
<tr>
<th>Run #</th>
<th>Seq. #</th>
<th>Q_{MoCO} (^d) (mg/min)</th>
<th>Press (mTorr)</th>
<th>Temp (°C)</th>
<th>RF (amps)</th>
<th>Plasma (Y/N)</th>
<th>R_{(100)} (%)</th>
<th>Dep. rate (mg/min)</th>
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<tr>
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<td>210</td>
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</table>

- Contains MoO\(_3\) (110) diffraction peak  
- Mo(CO)\(_6\) flow rate  
- Contains < 1% carbon (XPS)  
- Oscillating plasma
Table III  Experimental results for replicates and axial points

<table>
<thead>
<tr>
<th>Run</th>
<th>Seq.</th>
<th>$Q_{Mo(CO)}$</th>
<th>Press</th>
<th>Temp (°C)</th>
<th>RF</th>
<th>Plasma</th>
<th>$R_{10%}$</th>
<th>Dep. rate</th>
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<tbody>
<tr>
<td>#</td>
<td>#</td>
<td>(mg/min)</td>
<td>(mtorr)</td>
<td>(℃)</td>
<td>(amps)</td>
<td>(Y/N)</td>
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<td>(mg/min)</td>
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</table>

a - contains $\alpha$-MoO$_3$ (110) diffraction peak  
c- Mo(CO)$_6$ flow rate  
b - contains < 1 % C (XPS)

4.3 Further Depositions

Four runs 9, 11, 13 and 15 were replicated to assess the error in the PECVD process and four additional depositions were conducted at the axial points (Table III). The replicates indicate that there is little error at high values of temperature and pressure, but a variation in the response $R_{10\%}$ in runs 9 at 312.5°C and 210 mtorr was observed. The difference between the runs is in the intensity of the $\alpha$-MoO$_3$ (110) peak and increasing either the pressure or temperature as shown in runs 11, 13 and 15 increased the response.
Four depositions were conducted at axial points which are comprised of the center point settings for 3 variables and either increasing or decreasing the fourth variable. Under the centerpoint setting (i.e. run 17) the response is zero, yet by increasing temperature (run 23), increasing RF (run 21), increasing pressure (run 24), or decreasing Mo(CO)$_6$ flow rate (run 22) the response $R_{\text{okO}}$ increases.

### 4.4 Empirical Model

The relative importance of the variables was quantified by modeling the response using SAS$^{21}$, a statistical software package. The model consisted of four variables plus four interaction terms. A least squares regression analysis was performed with several linear models including one which had 15 terms. Only eight terms were significant at a 95% confidence interval$^{17}$, (Table IV) and they were included in the model [Equation (6)].

$$R_{\text{okO}} = 39.0 - 21.2X_{\text{QMo}} + 13.6X_p + 15.7X_T + 24.1X_{\text{RF}} - 12.1X_{\text{RF}}X_{\text{QMo}}$$

$$+ 9.9X_pX_T + 9.1X_{\text{QMo}}X_TX_{\text{RF}} + 11.1X_{\text{QMo}}X_pX_TX_{\text{RF}}$$  (6)

The model fit of the data is expressed in two ways. The $R^2$ value for the model is 0.939 (Table IV). This indicates that 93.9% of the variability in the data is predicted by the model. A perfect fit would have an $R^2$ of 1.0. The $F$ value for the model is 29.0 which gives an indication of the explanatory force of the model (Table IV). A model that did not have any explanatory force at a 95% confidence interval would have an $F_{(8,15)}$ value less than 2.77$^{17}$. 
The predicted values from the model, Equation (6), and experimental values were compared (Table V). The residual was determined by subtracting the predicted value from the actual response; the values of the residuals varied from -17.2 to 18.0 with the predicted values ranging from -14.8 to 116.2.

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<th>Mean Square</th>
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</tbody>
</table>

Adjusted $R^2 = 0.939$

<p>| Variable                  | Coefficient | Std. Error | T-Value | $P &gt; |T|$ |
|---------------------------|-------------|------------|---------|-------|
| Intercept                 | 39.8        | 3.04       | 13.1    | 0.0001|
| $X_{QMo}$                 | -21.2       | 2.97       | -7.15   | 0.0001|
| $X_p$                     | 13.5        | 2.84       | 4.77    | 0.0002|
| $X_T$                     | 15.7        | 2.90       | 5.45    | 0.0001|
| $X_{RF}$                  | 24.1        | 2.97       | 8.13    | 0.0001|
| $X_{RF}<em>X_{QMo}$          | -12.1       | 3.21       | -3.77   | 0.0018|
| $X_p</em>X_T$                 | 9.9         | 3.16       | 3.12    | 0.0070|
| $X_{QMo}<em>X_T</em>X_{RF}$      | 9.1         | 3.15       | 2.88    | 0.0113|
| $X_{QMo}<em>X_p</em>X_T*X_{RF}$  | -11.1       | 3.16       | 3.52    | 0.0031|</p>
<table>
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<tr>
<th>Run</th>
<th>Sequence</th>
<th>( R_{\text{MBD}} )</th>
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<th>Residual</th>
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<td>71.3</td>
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</tr>
<tr>
<td>24</td>
<td>28</td>
<td>85</td>
<td>66.9</td>
<td>18.0</td>
</tr>
</tbody>
</table>
5 DISCUSSION

5.1 LPCVD and PECVD Films

Thermodynamic equilibrium calculations for the Mo(CO)$_6$-O$_2$ system indicated that α-MoO$_3$ is the most stable solid compound formed from 127-527°C (page 41, from paper I). The gas phase composition under equilibrium conditions is predominantly CO$_2$ when O$_2$ is in excess. Under LPCVD conditions as exhibited for runs 1-8, 10, 12, 14, and 17-20, the deposits consist of reduced oxides, and the gas CO$_2$ concentration is low. The LPCVD films are thermally activated and controlled by the reaction kinetics as are most LPCVD processes. Only at high temperatures 425°C or high pressures are the LPCVD kinetics favoring MoO$_3$ formation (runs 23 and 24). The PECVD films for runs 9, 11, 13, 15, (16) 21, and 22 consist of oriented α-MoO$_3$, and the gas CO$_2$ concentration is higher than for LPCVD. The PECVD films are both thermally activated and plasma assisted by the electrical input of energy into the discharge.

For Mo films produced from LPCVD of Mo(CO)$_6$ the CO$_2$ content of the gas phase was related to the carbon content of the deposits according to the following reactions$^7$:

\[
\text{Mo(CO)}_6 \rightarrow \text{Mo(s)} + 6\text{CO} \quad (7)
\]

\[
2\text{CO} \rightarrow \text{C(s)} + \text{CO}_2 \quad (8)
\]

There appears to be a different mechanism for CO$_2$ formation in the molybdenum oxide formation because the PECVD films have a low carbon content yet the gas phase contains
A positive correlation exists between the CO₂ concentration in the gas phase and MoO₃ content of the film. For the PECVD MoO₃ deposits the CO₂ concentration was the highest, compared to the LPCVD MoO₃ films where the CO₂ content was lower but higher than for the reduced oxide LPCVD films. Olson deposited Mo₄O₁₁ films using an excimer laser from Mo(CO)₆, He, and O₂. According to mass spectrometry, Olson reported that the CO₂ gas phase content was too low to measure. The nature of the relationship between the phase composition and deposit composition is not understood but the gas CO₂ content may be attributed CO and O₂ reacting to form CO₂.

The plasma environment consists of ions, electrons, radicals, photons, and neutrals which facilitate the decomposition of the precursor and increase surface mobility. In order to form a plasma in presence of Mo(CO)₆, high energy electrons are needed in order to initiate and propagate the plasma. Other researchers have commented on the difficulty in sustaining a plasma on Mo(CO)₆ vapor alone and added either Ar or H₂ to stabilize the discharge. Argon is frequently added to PECVD and sputtering systems because it provides a source of electrons and is inert. Thus, it appears that high concentrations of Mo(CO)₆ in the gas phase inhibit plasma formation (runs 17-20). This can be overcome by increasing the RF current (run 21) or decreasing the Mo(CO)₆ concentration (run 22).

Comparing the PECVD and LPCVD responses indicated that oriented α-MoO₃ (0k0) films were produced at approximately 75-100°C lower temperatures in the presence of a plasma (runs 23 and 21). These results concur with a comparison study on W films between LPCVD and PECVD. The plasma allows for the deposition of crystalline films at lower temperatures because of surface bombardment which increases adlayer surface mobility and
plasma assisted partial decomposition of the precursor in the gas phase. The Mo(CO)$_6$ ionization potential is 8.3 eV$^{25}$ which is low in comparison to Ar at 15.3 eV and O$_2$ at 12.1 eV$^{26}$. Mo(CO)$_6$ does appear to decompose in the plasma and lead to deposition rates approximately 75% lower than the LPCVD case (calculated from results in Table II). This has also been observed for PECVD AlN deposits; at high RF power the reactant decomposed in the gas phase producing an AlN powder. The power had to be lowered in order to produce AlN films$^{27}$. The highly reactant nature of O$_2$ plasmas is well known; the process has recently been commercialized to decompose a gaseous metal halide to produce a metal oxide powder$^{28}$. Therefore, the RF current or RF power settings have to be carefully adjusted otherwise a powder will be produced instead of a film$^{27}$.

Separate studies comparing LPCVD and PECVD on Si and SiO$_2$ films showed that the influence of the plasma on the deposition depended upon the settings of the system pressure and temperature$^{29,30}$. At high values of temperature and pressure the deposition rate of PECVD films was lower than that of LPCVD films due to wall depositions$^{29,30}$. However, at lower temperatures the plasma activated the precursor decomposition and increased the deposition rate over LPCVD films$^{29}$. Therefore, the results of the LPCVD and PECVD comparison study depend upon the chemistry, process variables, and the variable settings.

5.2 Statistical Model

Modeling PECVD systems is difficult due to the process complexity. From the results in Table II and III a linear model was developed that consisted of eight terms (Equation 6). The significance of each term is indicated by either the magnitude of the coefficients, since
the standard errors are similar, or by comparing the T values (Table IV). Linear regression analysis indicated that RF current and Mo(CO)$_6$ flow rate had the largest effect on the response with temperature and pressure contributing to a lesser degree.

Several different models were considered. One model was considered that consisted of the four process variable terms only; it had an $R^2=0.77$. Adding the interaction terms increased the $R^2$ to 0.94. This means that when analyzing the overall system it is important to consider both the effect of variables and interactions.

The role of the process variables on the deposition process can be described. The Mo(CO)$_6$ flow rate controls the concentration of precursor in the gas phase which reacts to form molybdenum oxides. The system pressure influences the gas velocity, mean free path and residence time. The temperature affects the gas flow patterns, precursor decomposition, and the surface mobility of absorbed species. The RF current controls the energy levels of ions and electrons when a plasma is formed; it assists in the decomposition of the precursor and contributes to surface specie mobility.

Frequently in experimental design, the response is usually plotted as a function of the variables using a 3-D plot with the response on the z-axis and two variables on the x and y axes. Since there were four variables considered in this system, a generalized two dimensional plot was constructed that depicts the film deposition rate and response as a function of temperature and RF current (Figure 8).

The deposition rate is highest in the absence of a plasma and lowest in the presence of a plasma; this relationship is just the opposite for $R_{4010}$. There is a strong correlation between deposition rate and formation of (0k0) $\alpha$-MoO$_3$ as indicated by a Pearson correlation
coefficient of -0.8 (Figure 8). This indicates that the response and deposition rate go in opposite directions. The plot (Figure 8) also shows that the MoO$_3$ content of the film increases with the thermal or electrical energy input into the system.

The deposition rate was influenced by both the RF current (plasma) and Mo(CO)$_6$ flow rate and their interaction (Table IV). The plasma usually formed at Mo(CO)$_6$ of 1.00 mg/min with a high RF current and not at high precursor flow rates. It was not possible to compare the influence of high Mo(CO)$_6$ flow rates on the PECVD films because the discharge only formed at low precursor flow rates. The general shape of both responses are cubic expressions (Figure 8).

![Figure 8](image)

Figure 8  Plot of generalized deposition rate and $\alpha$-MoO$_3$ response versus temperature and RF current. The data was taken from depositions which had Mo(CO)$_6$ flow rates of 0.56, 1.00 and 1.44 mg/min.
The cubic shaped growth curve has been observed for other systems including GaAs and Si\textsuperscript{11}. For most systems there is a trade off between the deposit crystallinity/composition and high deposition rate\textsuperscript{31}. This was also observed for the \( \alpha \)-MoO\textsubscript{3} system.

The central composite design with a center point gives an indication whether the response is linear or quadratic as a function of the process variables. Comparisons of the actual response of the depositions with the predicted values for the model underestimate (< 0) the response at low levels and overestimate (> 100) the response at high levels (Table V). Since the minimum response is 0 and the maximum response is 100, it appears that a cubic expression may provide a better fit of the data. Modeling the response with a cubic expression was beyond the scope of this work. It was sufficient for this study to indicate which variables were contributing to the formation of \( \alpha \)-MoO\textsubscript{3} and determine their magnitude.

5.3 Comparisons with Reactive Sputtering

The closest equivalent system that the MoO\textsubscript{3} PECVD system can be compared to is reactive sputtering. The two systems differ in the source of the reactant but they both rely on a plasma to enhance chemical reactions. The formation of molybdenum oxides by reactive sputtering\textsuperscript{5,6} is strongly dependent on the target power which strongly influences the deposition rate and material composition. Statistical analysis of the LPCVD and PECVD MoO\textsubscript{3} films does indicate that the deposition rate and \( \alpha \)-MoO\textsubscript{3} orientation are negatively correlated which is in agreement with the sputtering results.
MoO$_3$ is the most oxygen rich of the molybdenum oxides and oriented films of it are primarily produced with the (0k0) orientation. As reported by Zou and Schrader for reactive sputtering of molybdenum oxides, when the target power is held constant, the crystalline orientation of the deposits are controlled by the substrate temperature as indicated.

\[
\begin{align*}
(110)\alpha\text{MoO}_3 & \rightarrow (010)\alpha\text{MoO}_3 \\
375^\circ C & \rightarrow 415^\circ C
\end{align*}
\]  

This same trend is exhibited by the PECVD results, that is

\[
\begin{align*}
(110)/(010)\alpha\text{MoO}_3 & \rightarrow (010)\alpha\text{MoO}_3 \\
269-312^\circ C & \rightarrow 387^\circ C
\end{align*}
\]  

but the temperatures are different (see Appendix B for films deposited at temperatures of 250-287°C). This is understandable due to the difficulty in obtaining an accurate surface reading in the sputtering system; the temperature reading can deviate ±30°C. As noted in the model, the process variables interact significantly so comparing temperatures alone is not sufficient enough to explain differences in orientation.
6 CONCLUSIONS

Statistical experimental design was used to develop a linear parametric model for the LPCVD and PECVD of (001) α-MoO₃ films. The technique indicated that all four process variables and interaction terms contributed to the formation of α-MoO₃. A linear model was used to describe the data although the data appears to fit a cubic model.

Comparing LPCVD and PECVD techniques under the same conditions indicated that crystalline α-MoO₃ films were produced at 75-100°C lower in the presence of a plasma. The films contained little carbon. It was demonstrated that a low frequency RF generator can be used to create a plasma for the deposition. The plasma formation was influenced by the RF current and the concentration of Mo(CO)₆ in the gas phase. The deposition rate of PECVD films was approximately 75% lower than LPCVD films. The formation of α-MoO₃ films and the deposition rate were negatively correlated.
REFERENCES


18. JCPDS - x-ray powder diffraction database
Three films were deposited at temperatures below 312°C which were not part of the original experimental design. The conditions under which the films were deposited are listed in Table BI.

<table>
<thead>
<tr>
<th>Run #</th>
<th>$Q_{Mo_6(CO)}$ (mg/min)</th>
<th>Press (mtorr)</th>
<th>Temp (°C)</th>
<th>RF (amps)</th>
<th>Plasma (Y/N)</th>
<th>Dep. rate (mg/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-38</td>
<td>1.00</td>
<td>280</td>
<td>287</td>
<td>30</td>
<td>YES</td>
<td>0.0567</td>
</tr>
<tr>
<td>S-40</td>
<td>1.00</td>
<td>280</td>
<td>269</td>
<td>30</td>
<td>YES</td>
<td>0.0543</td>
</tr>
<tr>
<td>S-37</td>
<td>1.22</td>
<td>280</td>
<td>250</td>
<td>30</td>
<td>YES</td>
<td>--</td>
</tr>
</tbody>
</table>

Characterization of the film deposited at 287°C with XRD indicated a peak at 3.805Å which is more intense than the (0k0) $\alpha$-MoO$_3$ peaks at 6.91, 3.46 and 2.31Å (Figure B1). This was also observed in the film deposited at 269°C. The film deposited at 250°C had a peak at 3.94Å which is attributed Mo$_7$O$_{14}$ in addition to MoO$_3$ diffractions. Raman and FTIR spectroscopy were used to analyze the films. The films deposited at 287°C and 269°C had a characteristic $\alpha$-MoO$_3$ Raman spectrum. However, the film deposited at 250°C had bands at 850 and 775 cm$^{-1}$, which are characteristic of $\beta$-MoO$_3$, in addition to $\alpha$-MoO$_3$ bands at 995, 819 and 282 and a Si band at 521 cm$^{-1}$. The FTIR spectra of all three films showed similar bands and confirmed the presence of $\alpha$-MoO$_3$ in the films; the films also contained a broad band from 480-460 cm$^{-1}$ (Figure B2).
Figure B1 XRD patterns of PECVD films deposited at (a) 250°C (b) 269°C and (c) 287°C
Figure B2 FTIR spectra of PECVD films deposited at (a) 250°C, (b) 269°C, and (c) 287°C, and (d) 312°C.
The change in orientation of α-MoO₃ from (0k0) at high temperatures to (0k0)-(110) MoO₃ at temperatures below 300°C is in agreement with previously reported reactive sputtering results. Olson reported that using Laser Raman spectroscopy at high laser powers it was possible to convert a Mo₄O₁₁ film into β-MoO₃ then α-MoO₃. So it is possible that the film deposited at 250°C may contain β-MoO₃ or it was converted by the laser beam. FTIR spectra of β-MoO₃ has not been published. The above films were relatively thin and poorly crystalline which explains for their weak intensity in Raman and XRD.

Further work is needed to investigate under what conditions is it possible to produce homogeneous β-MoO₃ using PECVD. To date β-MoO₃ has not been produced using PECVD; it has been produced using spray drying and reactive sputtering.
GENERAL SUMMARY AND RECOMMENDATIONS

Summary

The motivation for this research was to develop a LPCVD and PECVD system to produce α-MoO₃ films from Mo(CO)₆ and O₂. Both experimental design and one factor at a time experimental approaches were used to investigate the role of the process variables on the deposition. An experimental design approach was well suited for this project because of its complexity and many variables. Modeling the MoO₃ film formation as a function of the process parameters was a good starting point for understanding the molybdenum oxygen deposition process. The models indicated that all the process variables contributed to α-MoO₃ formation and the parameters act synergistically. It was demonstrated that a low frequency RF generator can be used to create an Ar-O₂ plasma and deposit crystalline MoO₃ films at lower temperatures than LPCVD. It was also discovered that there is a trade off between deposition rate, uniformity, and composition.

When using experimental design, care should be exercised in selecting the range of the process variables. If the levels are too broad, it is possible that a process minimum or maximum could be missed. Similarly, if the settings are too narrow the effect of a particular variable will be too small to be significant. It is also best to model process responses that are smooth and continuous. Therefore, experience gained from operating the system and from previous one dimensional searches should be considered when choosing process responses and variable settings.
Transport phenomena are considered part of the fundamentals of CVD that contribute to the film formation. Films deposited perpendicular to the gas flow were more uniform than the films deposited parallel to the gas stream. This was attributed to precursor depletion in the gas stream in the direction of flow and to differences in gas streamlines resulting from differences in reactor geometry. Computational fluid dynamics of horizontal deposition chambers indicate that deposition rate, uniformity and composition are dependent on the reactor geometry and gas velocity. At high substrate temperatures depositing films at high gas velocities is necessary to produce uniform films for a substrate that is parallel to gas flow\textsuperscript{14-17}. For the substrate perpendicular to the flow, gas velocity was not as important.

**Recommendations**

1. Replacement of the present rotary vane corrosive series pump with a 30-45 ft\textsuperscript{3}/min pump would double or triple the gas velocity. This would allow for a wider range of conditions to be investigated in future depositions and ultimately lead to uniform molybdenum oxide films.

2. Mo(CO)\textsubscript{6} is a molecule that consists of a Mo atom surrounded by six CO molecules. The Mo atom is bonded to the carbon atoms. It would be interesting to deposit molybdenum oxide films using a different precursor; preferably, one that has the molybdenum atom surrounded by oxygen species and that decomposes at higher temperatures than Mo(CO)\textsubscript{6}.
3. Adding an automatic pressure controller and motorized throttling value in the pump foreline would greatly increase the performance and control of the system and allow for greater reliability when depositing films.
REFERENCES CITED


