The reaction kinetics and film morphology of molybenum films deposited by LPCVD on a silicone surface
by Edward James Flanigan

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:
Molybdenum films were deposited by Low Pressure Chemical Vapor Deposition (LPCVD) on silicon substrates by the hydrogen reduction of molybdenum hexafluoride. The reaction kinetics were studied in order to determine a rate equation. Extensive scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (ESCA), auger electron spectroscopy (AES) and rutherford back-scattering (RBS) studies were conducted to characterize and analyze the morphology of the deposited molybdenum films.

The hydrogen reduction of molybdenum hexafluoride was determined to be one half order in hydrogen, approximately zero order in molybdenum hexafluoride and had an activation energy of 76,000 J/mol at temperatures from 250 to 3507deg;C, and total pressures from 0.9 to 10.0 torr. The preexponential factor was determined to be 2.02 x 106 nm s-1.torr -0.5.

The main features of the films were the high oxygen (up to 28%) and impurity content. Although pores could not be seen by the instrumental techniques provided, film impurities and surface roughness were attributed to a porous deposit. Rough interface conditions were explained by the competing silicon reduction reaction, and good quality deposits were seen to be produced at high temperatures and low pressures.

Results of this experiment were compared with previous studies involving tungsten and molybdenum LPCVD. One difference observed was the apparent lack of linear film growth with time. The other difference was that a molybdenum film had a resistivity of three times less than any previously reported resistivity for a LPCVD molybdenum film.

THE REACTION KINETICS AND FILM MORPHOLOGY OF MOLYBDENUM

FILMS DEPOSITED BY LPCVD ON A SILICON SURFACE

by

Edward James Flanigan

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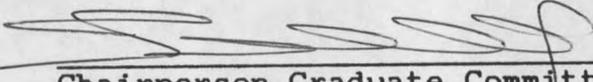Bozeman, Montana

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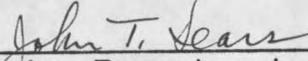APPROVAL

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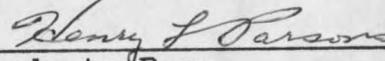
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ABSTRACT

Molybdenum films were deposited by Low Pressure Chemical Vapor Deposition (LPCVD) on silicon substrates by the hydrogen reduction of molybdenum hexafluoride. The reaction kinetics were studied in order to determine a rate equation. Extensive scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (ESCA), auger electron spectroscopy (AES) and rutherford back-scattering (RBS) studies were conducted to characterize and analyze the morphology of the deposited molybdenum films.

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The main features of the films were the high oxygen (up to 28%) and impurity content. Although pores could not be seen by the instrumental techniques provided, film impurities and surface roughness were attributed to a porous deposit. Rough interface conditions were explained by the competing silicon reduction reaction, and good quality deposits were seen to be produced at high temperatures and low pressures.

Results of this experiment were compared with previous studies involving tungsten and molybdenum LPCVD. One difference observed was the apparent lack of linear film growth with time. The other difference was that a molybdenum film had a resistivity of three times less than any previously reported resistivity for a LPCVD molybdenum film.

INTRODUCTION

In the semiconductor industry today, aluminum is a well known and important metal. This metal is used for contacts and interconnects in the microelectronics area of very large scale integration (VLSI). Competition in the semiconductor industry is growing at a rapid pace, though. This competitive condition brings about the need for a new metal with the capabilities of making smaller, less expensive and more productive components for integrated circuits.

Aluminum is the most widely used material for metallization of silicon devices due to its low room temperature resistivity and excellent adhesion to SiO_2 and other deposited silicate glasses [1]. However, aluminum has a relatively low melting point (660°C), and upon approaching this temperature the transfer of momentum from electrons is increased, causing transport, or migration, of the conductive material. This electromigration is a potential source of breakdown in aluminum interconnect lines [2,3].

The failures brought about by using aluminum has opened the door to new contact metals such as the refractory metals of molybdenum, tungsten and tantalum. Recently, molybdenum has shown potential applications not only as a contact or interconnect, but in other areas as well. Molybdenum silicides have been formed on refractory metals to protect Schottky diodes have been shown to approximate the ideal the

metal against high temperature oxidation [4-6]. Mo/Si
characteristic properties of Schottky diodes [7].
Molybdenum has been used for diffusion or corrosion barriers
and, because of its high ductility, for parts with complex
shape [8]. There has also been considerable interest in
molybdenum as a gate electrode for VLSI fabrication [9,10].

Molybdenum as a contact metal has shown promise in
VLSI because of its high melting temperature (2610 ^{O}C), high
corrosion resistance, low resistivity and expansion
coefficient that is close to that of silicon. A low
interconnect resistance and thus a high operating speed can
also be obtained by using molybdenum [10].

Today, modern surface science and other techniques
provide the capability of studying metal films designed for
use in microelectronics. These methods allow the researcher
to investigate such things as the uniformity and purity
throughout film deposits, the porosity of a deposited film,
and the condition of the interface after a metal is
deposited on a surface. This film morphology is greatly
affected by the deposition parameters and the rate of
deposition. In chemical vapor deposition (CVD), the main
parameters of the reaction are the substrate temperature,
the pressure of the reactant gas mixture and the ratio of

hydrogen to metal halide. The separate variation of these parameters has great influence on the deposition rate, on the amount of impurities, on the crystal structure and grain size, and on the number of micro-bubbles that may develop under certain circumstances along the grain boundary during the reaction [11]. Improved knowledge of the film morphology and the kinetics of the reaction may provide a more efficient metal contact and manufacturing process for the semiconductor industry.

Research on the low pressure chemical vapor deposition (LPCVD) of molybdenum is limited. Several studies used molybdenum pentachloride as the source of molybdenum [7,9,12-16]. Some studies have used the carbonyl as the source of Mo [17-20]. Schottky barriers or diodes were formed by selective deposition of molybdenum [7,21] and Mo layers have been formed on n-type polysilicon lines [22]. Other authors have studied the silicides formed by molybdenum deposition [23,24] or have studied molybdenum deposits for metallurgical applications which require high deposition rates, high temperatures and atmospheric pressures in order to cover a large area. A few authors have considered the hydrogen reduction of molybdenum hexafluoride for integrated circuit technology [25,26].

In this study, molybdenum was deposited on a silicon surface by hydrogen reduction of molybdenum hexafluoride.

This was performed over a temperature range of 250-350°C and a total pressure range of 0.9-10.0 torr. The objective of this research was to investigate the molybdenum film morphology and study the kinetics of the molybdenum deposition. The amount of deposition was determined by acid dissolution of the molybdenum films. This acid dissolution method was employed in determining a reaction rate equation. The film morphology was studied by Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES), Electron Spectroscopy for Chemical Analysis (ESCA) and Rutherford Backscattering (RBS).

BACKGROUND

Integrated Circuit Technology

Electronics basically began with the integrated circuit (IC) which was invented by Kilby in 1958 [2]. From the early primitive forms, IC's have evolved into complex electronic devices containing hundreds of thousands of individual components on a single chip of silicon.

The transistor is the most important component of an IC. This is what tells current to flow or not, or a circuit to open or close. One such type of transistor is the metal oxide field effect transistor (MOSFET) pictured in Figure 1. This has an n-type source and drain implanted in a p-type substrate. The letters n and p refer to negative and positive charge carriers, respectively. The source and drain are contacted by metal (e.g. Al or Mo) contacts and connected to a power supply. When a threshold voltage (V_T) is applied to the gate electrode, current flows between the source and drain. This voltage creates a field across the gate oxide which causes the adjacent p substrate to invert to n-type, thus creating a conductive n channel between the source and drain [2].

Importance of Molybdenum as a Contact or Interconnect Metal

Metallization, as described above, has many important

METAL CONTACTS

GATE
ELECTRODE

DEPOSITED
DIELECTRIC

FIELD
OXIDE

n⁺ SOURCE

GATE
OXIDE

n⁺ DRAIN

THRESHOLD
ADJUST
IMPLANT

p-TYPE
SILICON
SUBSTRATE

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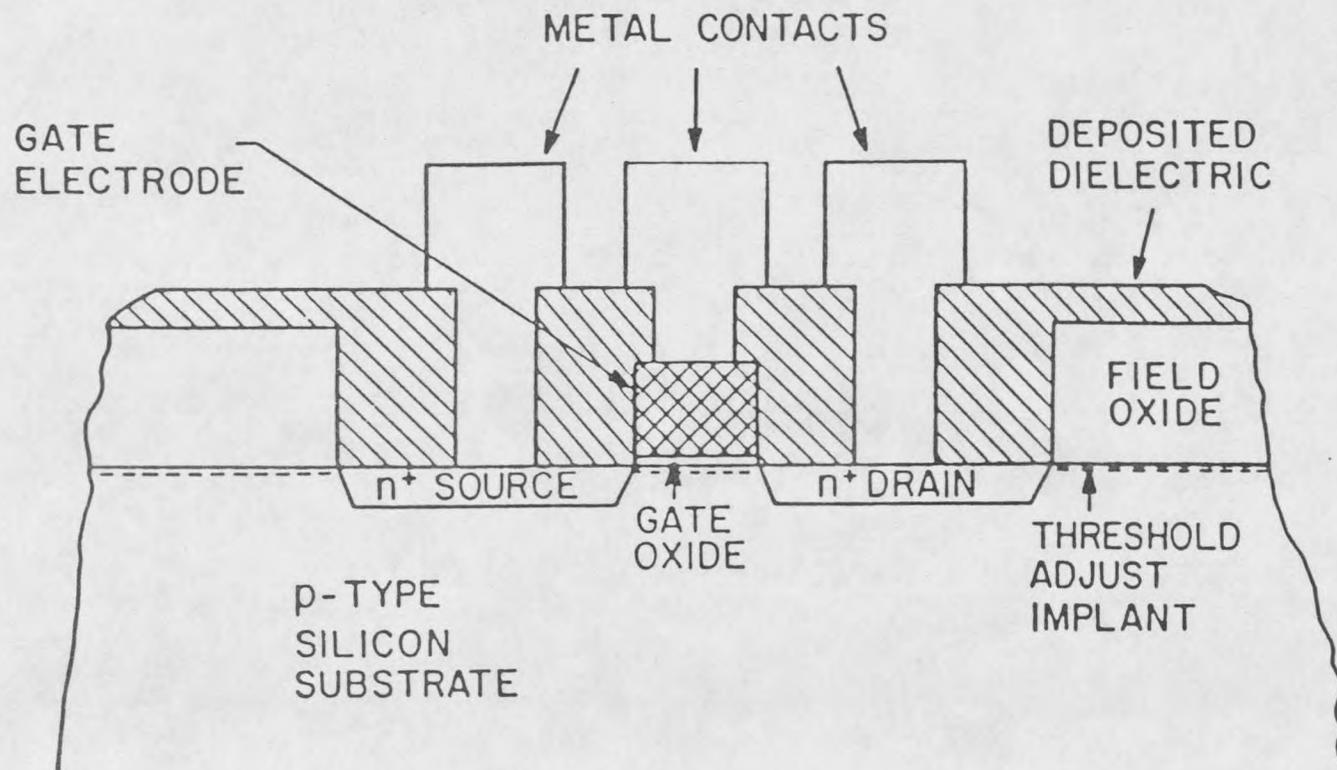
<u>Figure 1.</u> Schematic View of a MOSFET Cross Section

factors associated with the type of contact or interconnect used. Metallization requires a contact to have good mechanical properties, adhere firmly during both formation and subsequent processing, not cause excessive stress in the underlying semiconductor and have low electric resistance. A contact must also be compatible with the metal system used for the interconnection technology, not be susceptible to electromigration and corrosion, and, finally, be easily patterned by a straight forward process [3].

Most silicon MOS and bipolar integrated circuits now manufactured are metallized with Al or one of its alloys. Aluminum has high conductivity and excellent adhesion to both silicon and silicon dioxide. It also forms low-resistance contacts to p-type and heavily doped n-type silicon [1]. Despite these advantages, aluminum also has some problems in VLSI applications where junctions are shallow. Good step coverage is hard to achieve with aluminum. At the present time, physical vapor deposition is the only method available for depositing aluminum. It is very difficult to get the proper alloy composition to prevent junction spiking and electromigration. It is also difficult to obtain a low resistance contact for high speed switching. Thinner deposits produce higher current densities and higher resistances. Particulate interference, hillock formation and etching difficulty are also other problems which are explained in the literature [1,2].

Molybdenum, on the other hand, provides several advantages over aluminum mainly due to the method of deposition, CVD. With CVD low bulk resistivities, homogeneous films, better surface adhesiveness and smaller grained (large grains cause electromigration) films can be achieved. Also, CVD employs simple equipment and offers the capability of coating a large number of silicon wafers at a time relatively inexpensively. The most important advantage of using CVD molybdenum, however, is its improved step coverage and selectivity.

Molybdenum could be an excellent interconnecting metal because it can be selectively deposited on silicon leaving a silicon dioxide surface uncovered; therefore, the number of process steps can be reduced by eliminating lithography [2]. Lithography is the process of transferring geometric shapes on a mask to the surface of a silicon wafer.

Selective deposition of molybdenum eliminates some of the process steps in VLSI fabrication. The advantages realized by eliminating these process steps could result in a higher product yield and a substantial cost savings. Molybdenum is not without its disadvantages though. Under different sets of conditions, molybdenum was reported to produce high resistivity and porous films, a thermal expansion different from that of silicon and voids formed at the Mo-Si interface due to an undesired reaction with the underlying silicon.

Molybdenum Deposition (Basic Reaction)

Low pressure chemical vapor deposition of molybdenum from MoF_6 takes place by the following reaction:

$$MoF_{6(g)} + 3H_{2(g)} \rightarrow Mo_{(s)} + 6HF_{(g)}$$
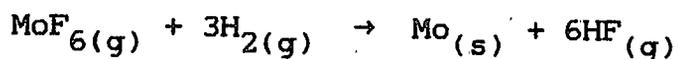
Another reaction that takes place some time during the hydrogen reduction of MoF_6 is the silicon reduction reaction:

$$2MoF_{6(g)} + 3Si_{(s)} \rightarrow 2Mo_{(s)} + 3SiF_{4(g)}$$
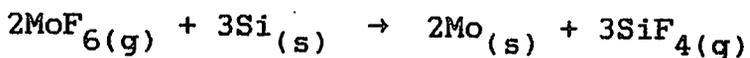
It is known that this reaction must take place sometime during the reaction process because during formation of the Mo layer some Si is consumed (about twice the volume of deposited metal) [25].

Free energy changes shown in Table 1 demonstrate that both reactions are thermodynamically possible [27]. The free energy change for the silicon reduction reaction show that this reaction is more favorable. Although the silicon reduction reaction takes place during Mo deposition, the intent of this research was to observe the hydrogen reduction reaction.

Table 1. Free Energy Changes for the MoF_6 Reaction

T = 300°C	H$_2$ Reduction	Si Reduction
ΔG^O (kcal/mol)	-65	-218

Hydrogen and Silicon Reduction of Molybdenum Pentachloride

Recent studies involving molybdenum stemmed from its possible use in microelectronics. A variety of molybdenum compounds have been used in studying the potential uses of CVD molybdenum. These include MoF_6, $MoCl_5$ and $Mo(CO)_6$. The literature on molybdenum carbonyl [$Mo(CO)_6$], however, showed this compound to be a poor source of molybdenum because of the incorporation of too much carbon in the films. Carbon-comtaminated films are unacceptable for use in microelectronic applications.

In Mo CVD investigations, molybdenum pentachloride ($MoCl_5$) is probably the most studied compound of molybdenum.

Hydrogen reduction of $MoCl_5$ has been accomplished at several temperatures and pressures in order to investigate molybdenum's possible uses in the production of various electronic components. Studies performed at low pressures of 3-15 torr with variable $MoCl_5$ and H_2 partial pressures and a temperature range of 700-1100 ^oC showed that by adjusting the deposition parameters, a thin, dense coating with good adhesion can be produced [15].

A similar study on Mo by the hydrogen reduction of $MoCl_5$ incorporated the same low pressure ranges and partial pressure ranges as the previous discussion but with lower temperatures between 500-800 ^oC [9]. This study was performed with the potential application of using the deposited molybdenum as a gate metal source in transitors. Here the deposition rate was thought to be controlled by surface reaction and was proportional to the 3/2 power of hydrogen partial pressure in the region of the surface. The films deposited in this temperature and pressure range had a thickness uniformity for a batch of 25 wafers within 5% and the films were not oxidized.

Molybdenum films deposited from $MoCl_5$ at atmospheric pressure and a temperature near 600 ^oC was another area of investigation [8,14]. These films were thick and of large grain size. The main interest in the atmospheric deposition studies was to examine the film resistivities as a function

of the purity of molybdenum chloride, poisoning contaminants and growth rate. Quite pure molybdenum films were found by H_2 reduction of $MoCl_5$ at atmospheric pressures. The factors that increased resistivity were found to be microcrystallinity and metalloid contamination. Impurities were MoO_2Cl_2 and incompletely reduced MoO_2 and MoO. Temperatures above 500 $^{\circ}C$ minimized the negative influence of oxygen.

Still another area of investigation using $MoCl_5$ as the source of Mo comes from the application of $MoSi_2$ films. Refractory metal silicides, such as $MoSi_2$, are also being studied as highly conductive interconnect and gate-electrode materials. This silicide ($MoSi_2$) is also being studied as a potential material in reducing the gate dimensions in I^2L (integrated injection logic) circuits [24]. Studies in this area all produced good quality, highly oriented thin films. The films may also be easily chemically dry etched and do not form hillocks. Molybdenum disilicide films are also resistant to HCl, HNO_3, H_2PO_4, H_3PO_4, and HF solutions.

Although hydrogen reduction of $MoCl_5$ produces high purity thin films, there are several disadvantages to this method of deposition. Most of the techniques reported excessive film resistivity [15]. There were also reports of unreasonable amounts of film contaminants [12]. The biggest disadvantage in using $MoCl_5$ is that at temperatures below

150 $^{\circ}$C, the chlorides condense on any surface. Molybdenum pentachloride also can not be obtained commercially and special equipment is needed to produce this gas. These last two disadvantages make MoF$_6$ as the source of Mo much more desirable.

Hydrogen and Silicon Reduction of Tungsten Hexafluoride

Molybdenum and tungsten chemistry is similar enough to expect similar CVD behavior. Tungsten deposition by the hydrogen reduction of tungsten hexafluoride for use in microelectronics is well known [32].

Kinetic work by McConica and Krishnamani, and Broadbent and Ramiller, showed deposition of tungsten from WF$_6$ is very similar to molybdenum deposition from MoF$_6$ [28,29]. They found hydrogen reduction of WF$_6$ to be 1/2 order in hydrogen and zero order in WF$_6$ with an activation energy of 69000 J/mol (0.71eV) at temperatures from 250 $^{\circ}$C to 500 $^{\circ}$C and pressures from 0.1 to 10 torr. The preexponential factor was determined by McConica and Krishnamani to be 6.2 X 10^4 nm/s·Pa$^{0.5}$. McConica's and Krishnamani's investigation also reported the rate limiting step could be either the addition of adsorbed monotomic hydrogen to adsorbed, partially fluorinated tungsten, or hydrogen fluoride desorption. However, Broadbent and Ramiller reported the rate limiting mechanism to be the Krishnamani, and Broadbent and Ramiller, also reported dissociation of H$_2$ adsorbed on the

surface.   McConica and   tungsten   to have a limiting
deposition thickness and   structure that was dependent upon
initial native oxide characteristics.   This condition was
observed in the absence of hydrogen, or in other words,
limiting depositions were   only   shown in the silicon
reduction reaction.   Other studies involving the low
pressure chemical vapor deposition of tungsten have reported
similar findings [1,8,30,31,32].

Hydrogen Reduction of Molybdenum Hexafluoride

As stated earlier, the information on LPCVD molybdenum
from the hydrogen reduction of MoF_6 is very limited. There
have been only two very recent studies that have conditions
somewhat similar to the research conditions utilized in this
research.

In a study by   Woodruff, et. al., Molybdenum was
deposited by hydrogen and silicon reduction of MoF_6 [26].
The temperature ranged from 200-500 ^{o}C, the pressure ranged
from 2-5 torr. The hydrogen flow rate was 100 sccm and the
MoF_6 flow rate range 5-25 sccm. Experiments for this study
were carried out in a hot wall, low pressure CVD reactor.
The MoF_6 was introduced by bubbling hydrogen through MoF_6.

It was found that the reaction was completely selective
against deposition on silicon dioxide.   The reaction with

silicon took place at a very high rate and was not self-limiting, in contrast to the analogous reaction between WF_6 and Si. To prevent the silicon reduction reaction with molybdenum and thus the severe etching of silicon, attempts were made to put a capping layer between the silicon and the depositing molybdenum. Films of selective CVD tungsten, and sputtered TiW and Mo were ineffective as barrier films to the MoF_6-Si reaction. More importantly, it was discovered that the Mo films deposited over silicon were high in oxygen content and porous.

A similar study by Lifshitz, et. al., was performed in a hot walled, tubular reactor at a temperature range of 200-400 ^{o}C and a pressure range of 0.2 to 0.9 torr [25]. Mo films were deposited at these conditions by LPCVD on silicon substrates by the reduction of molybdenum hexafluoride in hydrogen and argon atmospheres. The deposition proved to be extremely selective, with no Mo observed on silicon dioxide. Reduction by both hydrogen and silicon were shown to contribute to the deposition with approximately equal, extremely high deposition rates. No self limiting thickness was observed. Again the main feature of the deposits was extreme porosity - about 30%. The films grew in a loose, open structure which could be easily penetrated by reactant gases. This porosity was used to explain such things as high deposition rates, high resistivity and the continuing reaction of Si with the molybdenum hexafluoride reactant.

The only other existing study of LPCVD Mo by the hydrogen reduction of MoF_6 was performed by Schroff and Delval [8]. This study was not performed using a silicon substrates but rather using various substrates such as copper, stainless-steel and molybdenum. The deposition temperature ranged from 600 to 1100 ^{o}C and the pressure varied from 5 to 760 torr within a H_2/MoF_6 ratio of 1 to 60. This investigation was performed to study the dependence of the deposition thickness on the reaction parameters. The number of defects in the films were measured along with the amount of gaseous impurities, in particular, fluorine. It was found that bubble free coatings were obtained when the H_2/MoF_6 ratio was kept within the range of 3 to 6, the pressure kept below 20 torr and the temperature kept above 700 ^{oC}. Low fluorine content deposits were observed to lead to thermal instability.

Analyses by AES

Auger Electron Spectroscopy (AES) is a technique that may be employed in measuring the quality and quantity of CVD deposits. The technique is based on the Auger process. The Auger process itself is preceeded by an excitation process, which leaves an electron hole in a core level of an element. In this case, the preliminary excitation process is

stimulated by absorption of energy from a primary electron beam. After the excitation process, the core hole can be filled by an electron occupying a higher energy level, that is, either a shallower core level or a valence state. This electron must lose energy in the process and the energy is transferred to another electron. This last electron may receive enough energy to leave the system, thus becoming an Auger electron. Auger electrons are then detected by an analyzer that measures their energy.

AES can be used to conduct a depth profiling of the deposited molybdenum. The equipment used in AES depth profiling is equivalent to a standard Auger spectrometer except for the prescence of an ion gun. The ion gun is used to bombard the surface of the sample with ions of an inert gas, usually Argon. The bombardment removes the surface atoms of the sample at a slow rate [33].

If a quantitative Auger analysis is carried out stage by stage during interruptions in the ion bombardment, the results will give the composition of the sample at different depths with respect to the original surface. The depth of molybdenum on silicon can then be obtained from:

$$z = 3.6 \times 10^{-4} [M/\rho] j_p S.$$

where z equals the erosion rate in μm/hr, M is the atomic weight of the target atom in amu's, ρ is the density of the target in g/cm^3, j_p is the primary ion current density in μA/cm^2 and S is the sputter yield [33].

The Auger depth-profiling technique is affected by several factors like ion mixing, surface roughness, impurities in the ion beam, residual gas adsorption, oxygen content in the chamber, uneven current distribution, etc. These all contribute to poor depth resolution and accuracy. Further details on AES can be found in the literature [33,34].

Analyses by SEM

A very powerful tool in surface studies is scanning electron microscopy (SEM). This technique enables one to observe and analyze phenomena occuring from a scale of about 50 A to several centimeters. The scanning electron microscope not only permits analysis of very tiny objects, but also reveals the spatial or structural relationships between components analyzed [35].

In the scanning electron microscope, the surface to be analyzed is irradiated with a finely focused electron beam which is rastered across the surface of the specimen. The types of signals produced when the electron beam impinges on a specimen surface include secondary electrons,

backscattered electrons, Auger electrons, characteristic x-rays, and photons of various energies. Secondary emission electrons are preferred to the backscattered elctrons, as they provide higher contrast due to their enhanced emission in the case of rough surfaces [36]. The detector for secondary electrons is only sensitive to electrons that emerge from the specimen with less than 50 keV of energy [37].

The incident beam of electrons that scan the surface of the specimen is similar to that used in a television tube. A directly synchronized raster pattern is displayed on a cathode ray tube, and the intensity of the moving spot is modulated by the signal from the secondary electron detector. In other words, the brightness at any point on the screen will depend on the strength of the signal from the corresponding point on the specimen. In this way, an image of the specimen surface is built up on the CRT, point by point [38].

In using SEM techniques for film studies, information obtained from the secondary electron images is usually morphological. Morphological studies can be performed in several ways [39]. For deposition of metal (i.e. molybdenum) on a surface, a very useful technique is direct recognition of shape or crystal habit. If the system being analyzed is well known, it may be possible to recognize the

various constituents present and obtain an estimate of their relative size and concentration.

Scanning electron microscopy as a qualitative and quantitative technique is not without its flaws however. The operation of the equipment, the sample preparation and the interpretation of the instrument parameters are all very complicated. A very skilled and experienced technician is required to operate SEM equipment. Other factors that affect SEM results are specimen contamination, multiple scattering, channeling patterns, etc. These are explained in detail by Cocks [35].

Analyses by ESCA

Another technique used in the study of thin films is electron spectroscopy for chemical analysis (ESCA). ESCA, like AES, is a surface sensitive technique. ESCA also analyzes electrons released from a surface by their kinetic energies.

Impinging x-rays on a sample surface cause the emission of electrons by the photoelectric effect. The electrons are analyzed by their kinetic energy, and more importantly, their binding energy. The binding energy is determined by:

$$KE = h\upsilon - BE - \sigma_s$$

where KE is the kinetic energy of emitted electrons, hυ is the photon energy, BE is the binding energy of the electrons and σ_s is the spectrometer work function. The spectrometer work function and photon energy are known entities.

Like Auger electrons, the binding energy of the electrons in ESCA are characteristic of the element that produces them. This makes elemental identification possible. The binding energy also indicates the chemical bonding of an atom. For example, it can tell if an atom is combined with oxygen, flourine or other such impurities. This information aids in providing details on the surface chemistry of a film. Further details on ESCA may be found in the literature [40-44].

In analyzing thin films of molybdenum for possible electronic applications, the purity of the film is very important. ESCA analysis may be used in combination with ion sputtering to analyze successive film depths throughout a layer of molybdenum. Each element or impurity can be analyzed to see what chemical shifts or changes are taking place from the sample surface to the interface. Binding energy values for elements and compounds are tabulated in the literature [44]. From these values and their corresponding spectra, the chemical make-up of a film can be determined and also speculation can be made as to film porosity, resistivity, etc.

Analyses by RBS

Rutherford backscattering (RBS) is another technique used in CVD film analysis. This technique, similar to the previous ones, uses a beam of monoenergetic and collimated alpha particles (He-nuclei) to impinge perpendicularly on a target. This technique incorporates a high-energy beam of charged particles. The particles pass through a series of devices which collimate or focus the beam and filter it for a selected type of particle and energy.

When the high energy alpha particles penetrate the surface of a sample, some particles are implanted in the sample, some particles pass through the sample (in the case of a thin target) and other particles are scattered backwards at angles greater than 90° from the incident direction. These backscattered particles that impinge on the detector generate an electrical signal. This signal is amplified and processed by a computer. The data is then printed out in the form of a spectrum.

As in ESCA and AES, elemental identification is also possible in RBS since it produces spectra that are characteristic of the parent atom. However, the advantage of RBS resides in the speed of the technique, its ability to perceive depth distributions of atomic species below the surface without sputtering (ion sputtering can sometimes modify the sample and lead to erroneous conclusions), and the quantitative nature of the results. Further details on

RBS are available in the literature [45].

RBS in thin film studies is important in analyzing for film purity. Observation of an RBS spectra shows whether a film is pure (clean sharp peaks) or combined with other elements (interdiffusion of peaks). The information provided by an RBS spectra can be used in conjunction with ESCA and AES in confirming the chemical state of a deposited film.

RESEARCH OBJECTIVES

The objectives of this research are essentially two-fold:

1. Study the kinetics of the hydrogen reduction of molybdenum hexaflouride on a silicon surface.

2. Characterize deposited molybdenum films by AES, ESCA, SEM and RBS and compare the findings with those published in the literature.

EXPERIMENTAL EQUIPMENT

The stainless steel reactor system is diagramed in Figure 2. This low pressure chemical vapor deposition (LPCVD) system consisted of the following primary components: the gas flow control system, the reactor and heater, the chamber pressure control system, the pumping system, the trap system and the acid gas detection system. The contact substrate heater used in this system was designed such that the silicon wafer received a uniform heating distribution which is required for obtaining accurate kinetic data.

Gas Flow Control System

Hydrogen (99.9995% pure, Matheson Co.), helium (99.9999% pure, Matheson Co.) and molybdenum hexaflouride (99.9%) pure, SERAC Co.) flows were controlled by MKS type 1259 controllers. All the flow controllers were connected to a MKS 247B four channel readout and power supply unit. The gas flows in each channel were set independently, but could have been set as ratios of one another. The controllable gas flow ranges were 0-101 sccm/min for hydrogen, 0-145 sccm/min for helium and 0-21 sccm/min for molybdenum hexaflouride.
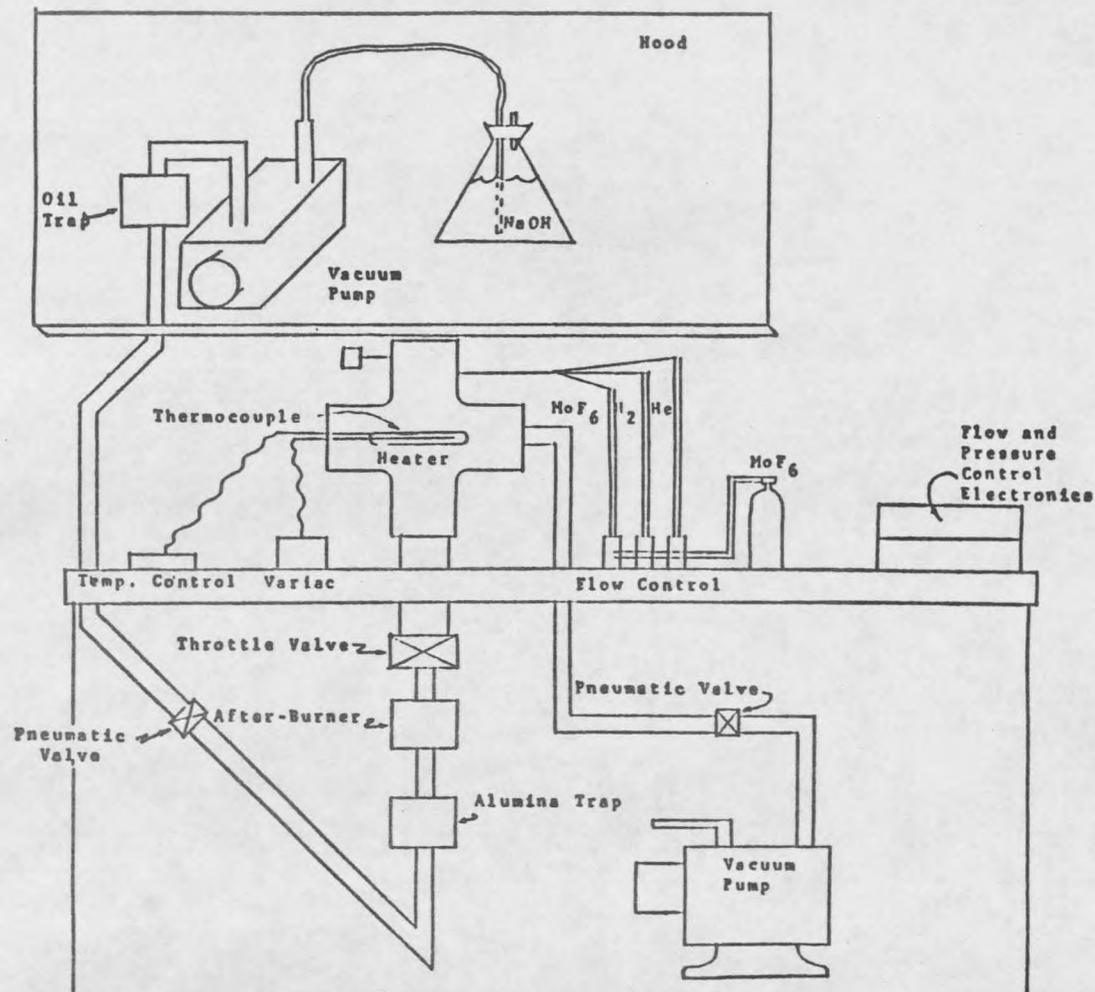
Figure 2.   LPCVD Reactor System

Reactor and Heater

The low pressure stainless steel reactor system (Figure 2) was wrapped with fiberglass heat tape to insure that water vapor inside the reactor was kept at a minimum. The reactor was accessed by a flange to which the substrate heater was attached. A 2.5cm X 3.5cm X 5.0cm stainless steel block was used as the substrate holder and heating unit. Centered in this block were four equally spaced ceramic tubes with Ni-chrome wire running through them (Figure 3). The wires were connected in a series arrangement and the total resistance of the system was 2.1 ohms. The leads for the Ni-chrome wires were attached to copper feed-throughs welded in the access flange. These copper feed-throughs were in turn connected to a variac power supply controller. The manually controlled heating arrangement was capable of temperatures up to about $500^{\circ}C$.

Two 1/4" stainless steel rods which were screwed into the feed-through flange acted as the support for the substrate holder. The underside of the substrate holder had two machined grooves for positioning this holder on the rods. The substrate holder was spot-welded to the rods.

Centered at the surface of the substrate holder was the Alumel-chromel thermocouple. The thermocouple wires were attached to larger diameter Alumel-chromel feed-throughs
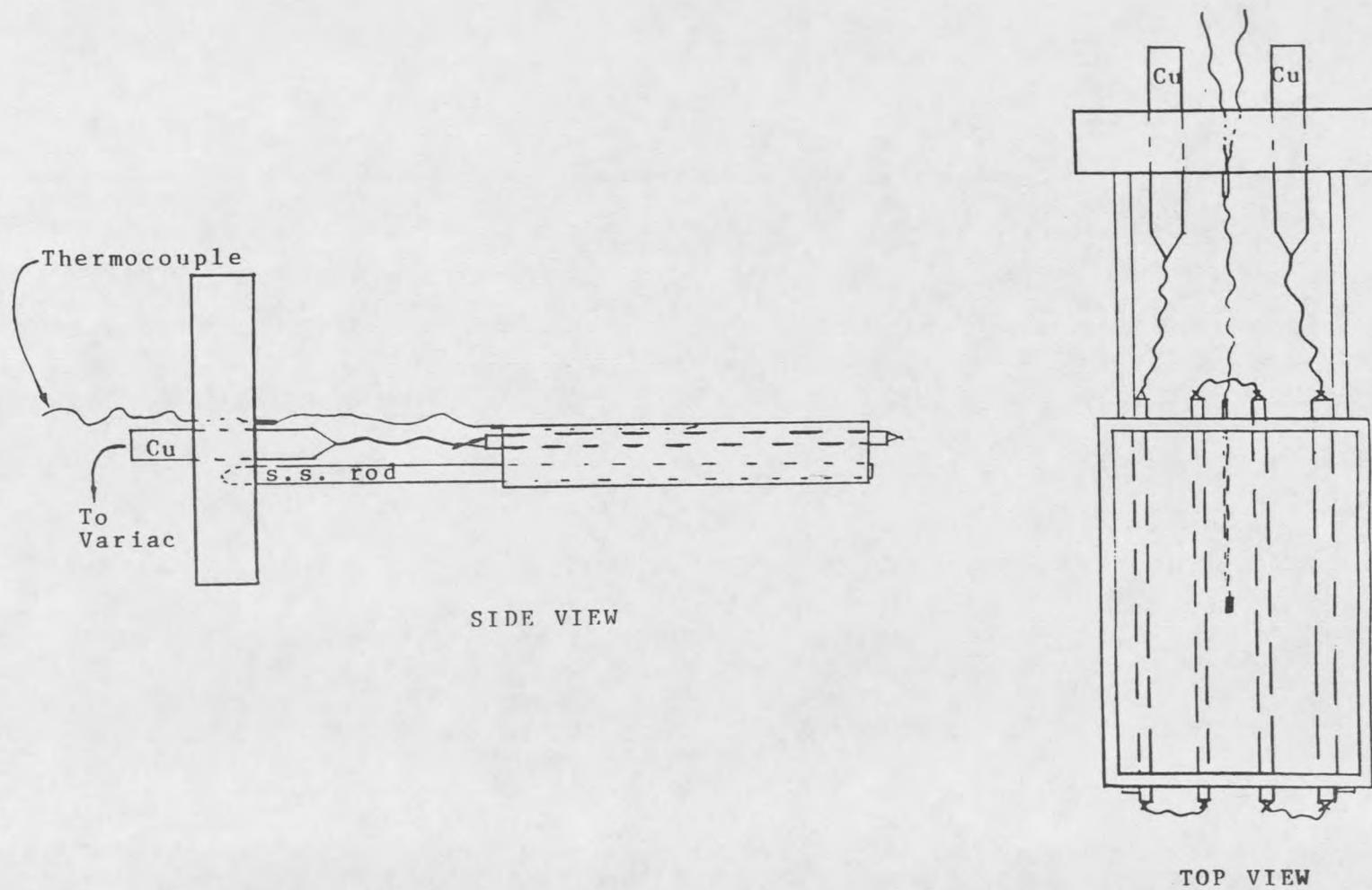
Figure 3. Substrate Heater/Holder for the LPCVD Reactor

which were welded in the access flange. The temperature was recorded by a digital thermometer and was manually controlled by varying the supply voltage through a variac.

Silicon slices were cut to fit into the top grooved portion of the substrate heater/holder.

Pressure Read-Out and Control System

The chamber pressure was sensed by an absolute capacitance manometer gauge, MKS baratron type 222B. This was mounted on top of the reaction chamber. The pressure was displayed on a MKS power supply and digital readout PDR-D-1.

A MKS throttle valve type 253-1-40-1 was quick clamped to the bottom of the reaction chamber. The throttling valve and pressure sensor were interfaced through a MKS exhaust valve controller type 253A. The chamber pressure was controlled by regulating the throttle valve opening and thus the pumping speed.

Pumping System

The pumping system consist of two mechanical roughing pumps connected in parallel. One pump (secondary pump) is a Precision vacuum pump, model D25. The pump sat on the floor below the reactor and evacuated directly from the reaction chamber. This pump has a maximum speed of 1500 l/s (0.88

CFM). The pump was used to achieve the initial vacuum of <
0.02 torr and was isolated from the system by a pneumatic
valve during the reaction. The other pump (primary pump) is
a Leybold-Heraues, model D4A, which has a maximum speed of
1500 l/s. This pump was located in a exhaust hood and was
the pump used during the reaction to exhaust the residual
reaction gases.

As stated earlier, the throttle valve was connected to
the stainless-steel reaction chamber. Between the throttle
valve and the mechanical pump located in the hood were two
residual gas traps, an oil trap and a pneumatic valve. The
pneumatic valve was a safety feature to protect the pump's
oil backstreaming in the lines in case of a power outage.
The other mechanical pump also contained this safety
feature. Both pneumatic valves were activated by
pressurized argon gas and were designed to fail closed.

Acid Gas Detection System

Since HF acid was one of the by-products of the reaction,
a sodium hydroxide neutralizing generator was set up in the
exhaust hood to neutralize HF gas. When the gases were
exhausted from the roughing pump in the hood, they were
bubbled through a sodium hydroxide solution where the acid-
base reaction took place leaving a sodium flouride
precipitate. Phenophthalein was added to the NaOH as an

indicator. The purple indicator turned clear if the solution became acidic.

The purpose of this acid neutralizing station was to provide an indication of how efficient the alumina trap system was in adsorbing the residual HF gas and to protect the pump from this gas. The NaOH solution was made very dilute. The procedure was to change the alumina trap each time a NaOH solution turned clear.

After-Burner and Alumina Trap System

A stainless steel, in-line after-burner and alumina trap were positioned between the throttling valve and the roughing pump located in the hood. The after-burner was a stainless steel can filled with stainless steel shavings. The can was wrapped with ceramic-insulated Ni-chrome wire. Another layer of fiberglass insulation was wrapped around the Ni-chrome wire and secured to the stainless steel can. The Ni-chrome wire was connected to a variac and kept at a constant temperature of around $300^{O}C$. Residual MoF_6 from the reactor was reduced on the heated stainless-steel surface.

Two copper rods mounted on a stainless-steel feed-through flange were quick-connected to the side of this after-burner and had spot-welded thermocouples in contact with the stainless shavings in the after-burner. This flange and