Silicon-reduced LPCVD reaction kinetics and film morphology of molybdenum on Si surfaces
by Chang Soo Park

Abstract:
Molybdenum films were deposited by low pressure chemical vapor deposition (LPCVD) on (100) oriented single crystal silicon substrates by the silicon reduction of molybdenum hexafluoride (MoF6). The dependence of film thickness on deposition parameters such as temperature, total pressure, and deposition time was studied. Scanning electron microscope (SEM) and Auger electron spectroscopy (AES) were utilized to characterize the morphology of the deposited molybdenum film.

The silicon-reduced Mo films were found to be self-limiting at different thicknesses depending on the temperature and the total pressure. The film thickness at high temperatures was decreased by the severe etching, indicating the erosion of the Mo film.

The sheet resistance measurement of the films above 200 nm in thickness was found to be lower than 100 Ω/square. The film non-uniformity was also observed by measuring sheet resistance at different locations on the film, which was confirmed by SEM micrographs of the film surface.

The major impurities captured in the films were oxygen, fluorine, and carbon. The oxygen content was high when the films were not thick. High fluorine content was detected at the outermost layer of the films. This suggested that unreacted MoF6 gas or its subfluorides and decomposed fluorine atoms from adsorbed MoF6 would be the major source of fluorine at the surface.

By comparison with the literature, the findings of this study show similarities between silicon-reduced W and Mo films in aspects such as impurity content, porosity, and deposition kinetics.

SILICON-REDUCED LPCVD REACTION KINETICS AND FILM

MORPHOLOGY OF MOLYBDENUM   ON Si SURFACES


by

Chang Soo Park




A thesis submitted in partial fulfillment
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APPROVAL

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Chang Soo Park

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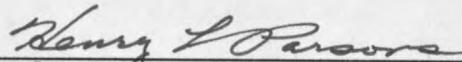Date

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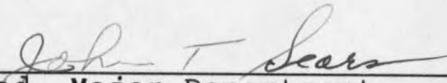
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## ABSTRACT

Molybdenum films were deposited by low pressure chemical vapor deposition (LPCVD) on (100) oriented single crystal silicon substrates by the silicon reduction of molybdenum hexafluoride ($MoF_6$). The dependence of film thickness on deposition parameters such as temperature, total pressure, and deposition time was studied. Scanning electron microscope (SEM) and Auger electron spectroscopy (AES) were utilized to characterize the morphology of the deposited molybdenum film.

The silicon-reduced Mo films were found to be self-limiting at different thicknesses depending on the temperature and the total pressure. The film thickness at high temperatures was decreased by the severe etching, indicating the erosion of the Mo film.

The sheet resistance measurement of the films above 200 nm in thickness was found to be lower than 100 $\Omega$/square. The film non-uniformity was also observed by measuring sheet resistance at different locations on the film, which was confirmed by SEM micrographs of the film surface.

The major impurities captured in the films were oxygen, fluorine, and carbon. The oxygen content was high when the films were not thick. High fluorine content was detected at the outermost layer of the films. This suggested that unreacted $MoF_6$ gas or its subfluorides and decomposed fluorine atoms from adsorbed $MoF_6$ would be the major source of fluorine at the surface.

By comparison with the literature, the findings of this study show similarities between silicon-reduced W and Mo films in aspects such as impurity content, porosity, and deposition kinetics.

## INTRODUCTION

As electronics technology moves toward the level of very large scale integration (VLSI), the requirements for the interconnect metallization become increasingly stringent. The current technology, using sputtered aluminum may well not be sufficient to meet the requirements. Step coverage, electromigration, hillocking, and eutectic formation with silicon are all serious problems of concern associated with aluminum alloy metallization. While various alloys and the introduction of diffusion barriers may alleviate some of the difficulties, the ultimate resolution of these concerns is by no means assured.

New materials for the alternative metallizations in use and under consideration in the industry are refractory metals, of which the two most commonly investigated materials are molybdenum and tungsten. These metals have much higher melting points than silicon, and their thermal expansion coefficients are similar to that of silicon. Molybdenum and tungsten are inert to both hydrofluoric acid and phosphoric acid. These properties attracted the attention of many workers in early days of large scale integration (LSI) technology [1]. Especially, chemical

vapor deposition (CVD) of these metals is an attractive process because this process can satisfy a variety of requirements for metallization, such as a diffusion barrier to prevent shallow junction spiking; low contact resistance to both $n^+$ and $p^+$ silicon; conformal step coverage of the metal (or, alternatively, a contact-refilling scheme) for planarizing vertical contacts; and contact electromigration resistance to accommodate the higher current densities in the submicron domain.

While many studies [2-10] were performed on the formation kinetics and the microstructures of CVD W films on Si by the reactions via hydrogen and silicon reduction of tungsten hexafluoride ($WF_6$), only a few studies [11,12] have been recently made on hydrogen-reduced Mo films by low pressure chemical vapor deposition. Furthermore, an extensive kinetic study of silicon reduction of $MoF_6$ has not been reported up until now. However, it is generally known that silicon reduction must take place first during Mo deposition process on account of its thermodynamic stability at the operating temperatures of CVD Mo [13]. In particular, it is important to understand the $MoF_6/Si$ reaction because this reaction defines the contact resistance, the degree of film adhesion, and other parameters related to the metal/silicon interface.

The existing diagnostic techniques that find wide use in semiconductor applications offer great opportunities for identifying and characterizing the morphology, chemical composition, and crystallographic structure of a deposited film. These factors important in the fabrication of microelectronics are greatly affected by the deposition parameters and the rate of deposition. The study of the deposition parameters is of great importance for the realization of reliable coatings when long life operation is to be expected. The main parameters of the silicon reduction reaction in CVD are the substrate temperature and the total pressure of the metal halide and inert gas. The separate variation of these parameters have great influence on the crystal structure, the amount of impurities, and grain size, and on the number of micro bubbles that may develop under certain circumstances along the grain boundary during the reaction [14].

In this study, molybdenum was deposited on a silicon surface by silicon reduction of molybdenum hexafluoride. This was performed over a temperature range of 250-400$^\circ$C and a total pressure range of 1-10 torr. The objective of this research was to study the kinetics of the silicon reduction reaction of molybdenum hexafluoride on a Si surface and investigate the dependence of the impurity concentration and

the film morphology on the deposition parameters.  An acid
dissolution method was utilized to measure the amount of the
Mo film deposited.   The film morphology and the impurities'
contents were investigated by the modern surface science
techniques: scanning electron microscopy (SEM), and Auger
electron spectroscopy (AES).

BACKGROUND

## New Metals for Metallization

Very large scale integration (VLSI) and the continued evolution of smaller and smaller devices has aroused concern about the existing metallization schemes and interest in the development of new metallization schemes for gates, interconnections, and ohmic contacts, and has motivated continued study of the reliability of aluminum and its alloys as current carriers.

The applicability of any metallization scheme in VLSI depends on several requirements such as low resistivity, good adherence, stability throughout processing, and good device characteristics and lifetimes. Most important of these requirements are the stability of the metallization throughout the integrated circuit (IC) fabrication process and its reliability during the actual use of the devices [15].

In the semiconductor industry, aluminum is a well known and important metal. This metal is most widely used for metallization of silicon devices such as contacts and interconnects in the VLSI devices due to its low room temperature resistivity and excellent adhesion to $SiO_2$. However, aluminum has a relatively low melting point

($660^0$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. Also, good step coverage is hard to achieve with aluminum because 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 as well. Particulate interface, hillock formation and etching difficulty are also other problems which may be encountered during processing.

On account of a rapid growth in the semiconductor industry of today, 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. The problems brought about by using aluminum have also accelerated the need for a potential new contact metal such as 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. For example, molybdenum has been used for diffusion or corrosion barriers due to its high ductility, and for parts with complex shape.

There has also been considerable interest in molybdenum as a gate electrode for VLSI fabrication.

Molybdenum could be an excellent interconnecting metal because it can be selectively deposited on silicon; no deposit occurs on the $SiO_2$ layers [16-18]. Therefore, the number of process steps can be reduced by eliminating lithography that is the process of transferring geometric shapes on a mask to the surface of a silicon wafer. If the selective molybdenum deposition process is proven reliable and reproducible, this process will probably be the best for multilevel structures as well as for contact metallization.

## Reactors for Chemical Vapor Deposition (CVD) of Mo and W

The first distinction between reactor types is whether they are hot-wall or cold-wall reactors, and this is dependent on the method used to heat the wafers. When radiant heating from resistance-heated coils surrounding the reaction tube is utilized, not only the wafers but also the reaction chamber walls become hot, and hence such designs are known as hot-wall reactors. In these systems, film forming reactions (and as a result, film deposition) occurs on reaction chamber walls as well as on substrates. If

the energy source is mounted within the reactor to primarily heat the wafers and susceptor, and not to cause appreciable heating of the reaction chamber walls, systems heated by this method are termed cold-wall reactors. In some cold-wall systems, however, significant chamber wall heating can still take place, and provisions for cooling the walls must be implemented (e.g. by water cooling) to prevent reactions or depositions from occurring there [19].

The next criterion used to distinguish reactor types is their pressure regime of operation (atmospheric pressure or reduced pressure reactors). Atmospheric pressure CVD reactors (APCVD) were the first to be used by microelectronics industry [20,21]. Hence, most CVD refractory metals' work for VLSI in early days was done in cold-wall reactors operating at atmospheric pressure since operation at atmospheric pressures kept reactor design simple and allowed high film-deposition rates. APCVD, however, is susceptible to gas phase reactions, and the films typically exhibit poor step coverage. Currently, atmospheric reactors are primarily used for low-temperature oxide (LTO) deposition and epitaxy.

Low pressure chemical vapor deposition (LPCVD) in some cases is able to overcome the uniformity, step coverage, and particulate contamination limitations of early APCVD systems

[22-24].    By operating at medium vacuum (0.25-2.0 torr),
and    higher    temperatures    (550-600$^{\circ}$C),    LPCVD    reactors
typically deposit films in the reaction-rate limited regime,
since at reduced pressure the diffusivity of the reactant
gas molecules is sufficiently increased so that mass-
transfer to the substrate no longer limits the growth rate.
The elimination of mass-transfer constraints in reactor
design increases the wafer throughput capacity of the
reactor.    Low pressure operation also decreases gas phase
reactions, making LPCVD films less subject to particulate
contamination.    LPCVD is used for depositing many types of
films, including Mo, W, poly-Si, $Si_3N_4$, and $SiO_2$ [19].
Especially, LPCVD of tungsten is currently under intense
investigation for its potential application in VLSI
circuits.    Applications investigated include shunting of
polycrystalline silicon gate and interconnect lines of
tungsten and molybdenum films with a lower resistivity to
reduce the resistance and capacitance (RC) time constant
[25,26] associated with interconnection paths, formation of
a barrier between silicon and aluminum to reduce aluminum
spike-induced failures [26,27], planarization of the
multilevel interconnect process [27,28], low resistance
contact formation to drain and source regions [25,27], and
formation of a Shottky barrier p-channel metal oxide silicon

(MOS) transistor to form latch up-free complimentary metal oxide silicon (CMOS) [27].

Plasma-assisted depositions provide films at very low sample temperatures. They do this by reacting the gases in a glow discharge, which supplies much of the energy for the reaction. Although the electron temperature in the discharge may be near $10^5$°C, the sample temperature is between 100 and 400°C. By using this technique, a large number of inorganic and organic materials have been deposited but only two are useful in VLSI technology: plasma deposited silicon nitride (SiN) and plasma-deposited silicon dioxide [29]. Due to undesirable incorporation of the impurities such as hydrogen, nitrogen, and oxygen, this technique is not useful for high purity deposition of thin metal films necessary for VLSI fabrication.

As described earlier, molybdenum and tungsten were most commonly investigated for VLSI technology. These metals can be patterned to serve as diffusion masks [29]. LPCVD of molybdenum, especially, provides several advantages over aluminum besides those of molybdenum stemming from high melting temperature (2610°C), high corrosion resistance, low resistivity, and an expansion coefficient that is close to that of silicon. The attractiveness of LPCVD of Mo for metallization comes from the conformal nature of coating

(i.e., good step coverage), the ability to coat large numbers of substrates at a time, the relatively simple equipment, and higher purity deposits. If the attractiveness is proven by further research, low interconnect resistance and a high operating speed can routinely be obtained by using LPCVD of Mo.

## Reaction Schemes of Film Deposition (Mo,W)

The chemical vapor deposition of Mo on Si, using $MoF_6$ as the source, can involve two reactions. The first reaction, the Si reduction of $MoF_6$, also known as the displacement reaction, involves consumption of Si:

$$2MoF_6 \text{ (g)} + 3Si \text{ (s)} \text{ ------>} 2Mo \text{ (s)} + 3SiF_4 \text{ (g)}$$

where (g) and (s) are gas and solid phases, respectively. Even when hydrogen is present, this reaction will always occur first. Thicker Mo films can be grown on the Si-reduced Mo film by $H_2$ reduction of $MoF_6$ according to a second reaction:

$$MoF_6 \text{ (g)} + 3H_2 \text{ (g)} \text{ ------>} Mo \text{ (s)} + 6HF \text{ (g)}$$
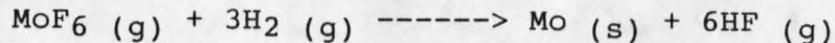
It is generally believed that molybdenum and tungsten chemistry is similar enough to expect similar CVD behavior. Kinetic work by Broadbent and Ramiller [5] and Sahin et al. [11] showed that deposition of tungsten from $WF_6$ was very similar to molybdenum deposition from $MoF_6$. Free energy

changes shown in Table 1 indicate that both $MoF_6$ reactions are thermodynamically possible [13] and the silicon reduction is more favorable.

Table 1. Free Energy Changes for $MoF_6$ Reactions to Form Mo

| Temp. | $\Delta G^O$ (kcal/mol) $H_2$ Reduction | $\Delta G^O$ (kcal/mol) Si Reduction |
|---|---|---|
| 400°C | -50 | -213 |

Although the great majority of CVD Mo films for IC applications are deposited by $H_2$ reduction, it is important to emphasize that the displacement reaction will always take place first. Therefore, it is the Si reduction reaction that determines the nature of the Mo/Si interface. This interface will determine such important device characteristics as contact resistance and leakage current, and such physical characteristics as interfacial smoothness and silicide formation kinetics [6].

## Si Reduction of $MoF_6$ and $WF_6$

In order to achieve good contact between silicon and metal a clean interface is essential. In the case of CVD

selective tungsten deposition the cleanliness of the interface is attributed to the initial phase of the deposition by silicon reduction of $WF_6$. During that phase only 100-200V are consumed while leaving a clean silicon surface, which makes good contact with the deposited metal. The tungsten deposited inside the contacts can be used as a contact barrier to protect underlying junctions from aluminum spiking and improve the electromigration resistance of the contacts [30].

This reaction deposits a thin layer of tungsten while consuming some of the exposed silicon. This reaction stops after tungsten film continuity is achieved, which is known as the self-limiting, as it acts as a physical diffusion barrier between the silicon and the $WF_6$. While many researchers have agreed with this phenomena, there still exist some discrepancies among the results published by now. For instance, in a study by McConica and Krishnamani [31] the thickness was found to be self-limiting in every case, and independent of time, temperature, and partial pressure of $WF_6$. The experiments were carried out for temperatures ranging from 250 to 375°C and partial pressures of $WF_6$ ranging from 66 to 664 Pa. The deposition time was varied from 1 to 20 minutes. Moriya and Itoh [32] also carried out the silicon reduction reaction in a low pressure region

of 0.1-0.2 torr for a temperature range of 150-600°C. However, they reported that the W films self-limited at different thicknesses, depending on the substrate material and the deposition parameters; the deposition temperature, the partial pressure of $WF_6$, and the total pressure.

Conventional wisdom in the CVD W deposition has stated many times that the Si displacement reaction results in thin (~10nm), self-limiting films of W. However, Tsao et al. [10] have seen silicon-reduced W films as thick as ~200nm and Mianowski et al. [33] have seen similar films up to 800nm thick in a linear relation with the deposition time when deposited in $N_2$ ambient gas at atmospheric pressure. An unusual temperature dependence of W film growth by Si reduction was also reported by Green et al. [6]. According to their results, films deposited below 310°C self-limit at about 6nm of full dense W. In a temperature range of 320 to 450°C, film thicknesses up to ~95nm were observed. In the higher temperature range, 500 to 700°C, film thicknesses of about 200 V were observed. This type of unusual decrease in thickness may result from a slow etching of the films (~0.4nm/min) by $WF_6$ [10]. To explain the temperature dependence and the self-limiting behavior of film growth (regardless of the ultimate film thickness at which the film self-limits), it was proposed that the rate-controlling step

would be a surface-catalyzed reaction. Thus, the temperature dependence of the sticking coefficient of a reactive intermediate probably controls the reaction.

The microstructures were studied for silicon-reduced W films deposited between 210 and 700°C [6]. In this study it was observed that the silicon-reduced W films were porous and discontinuous, and each grain was composed of tiny particles separated by a fine pore network. The grains were therefore "spongy", and reminiscent of a partially sintered mass of particles. Especially, the percentage of space occupied by trapped gases, pores, and inclusions in the CVD W films, ranging from 40 to 58.8%, accounts for the reduced density of the deposited films than that of bulk tungsten.

The impurity content obtained from Auger depth analysis by Tracy [8] showed that oxygen, fluorine, and carbon impurities were low; the profiles also indicated that most oxygen laid at the Si/W interface. The oxygen percentage in the silicon-reduced films obtained from XPS(X-ray Photoelctron Spectroscopy) analysis was found to be up to ~30% [31]. The microstructure of the deposited layer was found to be similar with surface oxide characteristics [10,34] since some oxygen in the native oxide layer on the silicon surface may incorporate during film formation.

Kinetic data on the silicon reduction of molybdenum hexafluoride is rare. In a few studies it was reported that the Mo film growth via the silicon reduction does not self-limit at all and furthermore the rate of reaction with silicon was very high. A kinetic data by Lifshitz et al. [35] showed that molybdenum films grew linearly with time with high deposition rate (~100nm/min), whereas tungsten ceases growth after the deposition of a relatively thin film. Woodruff and Sanchez-Martinez [12] also observed very thick films of molybdenum (up to 9.2 microns) for just the $MoF_6$/Si reaction. An interesting feature reported in the study [35] was the incubation time that precedes deposition. This incubation time was shorter for higher deposition temperatures and for hydrogen containing reactant gas streams. Clearly, the deposition rates strongly depend on temperature. According to the results the films formed at 250°C were an order of magnitude thicker than the films deposited at 200°C.

As stated earlier, the kinetic data on LPCVD molybdenum from the silicon reduction of $MoF_6$ is very limited because there has been no comprehensive and independent study on the kinetics. Studies by Woodruff and Sanchez-Martinez [12], and Lifshitz et al. [49] only included brief kinetic data of the silicon reduction reaction.

Despite the difference in the growth kinetics between Mo and W films, the morphology of Mo and W films exhibited many common features. First, it was reported that the films deposited over silicon were porous, separated in some cases at the grain boundaries, and had a high oxygen content distributed uniformly through the film, resulting in a high sheet resistance [35]. It is generally believed that such porosity of the films allows reactants and products to move freely to and from the silicon/metal interface, and the amount of the oxygen in the films depends on the temperatures at which the reactor was opened to air.

Second, it was reported that the metal-silicon interfaces look similar, with characteristic protrusions densely covering the interface [36]. Especially, these protrusions were considered to be the precursors of "tunnel effect", or "wormholes", which have been observed mainly in hydrogen-reduced W films [9,37,38], and in silicon-reduced Mo films [39].

## Hydrogen Reduction of $MoF_6$

The information on CVD molybdenum from $MoF_6$ is so limited because in the early days much more work was carried out for CVD of Mo from the chloride [40-43] and from the carbonyl [44,45]. The primary concern of most of these

studies was to investigate possible uses of molybdenum in the production of various electronic components. In addition, these two compounds were reported to be inadequate for a molybdenum source in the VLSI fabrication process because the literature on carbonyl showed the incorporation of too much carbon in the films and the disadvantage in using $MoCl_5$ is that at low temperatures below 150$^{\circ}$C the chlorides condense on any surface.

Similar to the kinetics of the $H_2$ reduction of $WF_6$, the kinetics of the $H_2$ reduction of $MoF_6$ showed the rate of molybdenum deposition to be a square root dependence on the hydrogen partial pressure and no dependence on the $MoF_6$ partial pressure over a temperature range of 250-350$^{\circ}$C and a total pressure range of 0.9-10.0 torr [46]. From an Arrhenius plot for reciprocal temperature versus r (rate of deposition) for total pressure of 0.9 and 5.0 torr and for total deposition times of five and ten minutes, an average activation energy was determined to be 76,000 J/mol. A statistical average of the values of all the preexponential factors was calculated to be 2.02 x $10^6$ nm/s torr$^{-0.5}$.

In a study by Shroff [47], the molybdenum films were deposited at temperatures of 600 to 1300$^{\circ}$C and at pressure of 0.01 to 760 torr on various substrates such as copper, stainless steel, and molybdenum. The influence of the

pressure on the deposition characteristics of molybdenum and tungsten was found to be similar. They suggested that the mechanism of the growth was due to the combined effect of the pressure and the temperature. In the case of Mo at low temperature and low pressure in the early stages of the reaction there was a slight etching of the base material, especially when it was molybdenum by the molybdenum hexafluoride or its decomposed sub-products.

The molybdenum film characteristics are also dependent on the deposition conditions. Sahin et al. [11] reported a significant amount of oxygen, fluorine, and carbon in the molybdenum films. A study by Woodruff and Sanchez-Martinez [12] was performed to investigate the quality of CVD Mo film from $MoF_6$ at low temperatures and pressures. They observed that the films deposited over silicon are porous and have a high oxygen content. In particular, it was shown that the Mo-Si interface was rough, indicating that Si reduction reaction took place.

In a study by Chen et al. [48], polycrystalline molybdenum films, 500V in thickness and 50-150nm in grain size, were chemical vapor deposited on (100) oriented, n-type silicon substrate heated to 650-700°C in hydrogen ambient. Ion beam-induced interfacial reactions in molybdenum thin films were investigated using transmission

electron microscopy (TEM), with which they found hexagonal $MoSi_2$, tetragonal $MoSi_2$, and hexagonal $MoSi_3$, mainly formed along grain boundaries. This was also found by in-situ annealing of the thin foil at 700°C for 2h in the electron microscope. They concluded that the observations may provide direct evidence of the important role of grain boundary diffusion in the formation of silicides.

## Hydrogen Reduction of $WF_6$

Many studies have been performed to investigate the kinetics of the hydrogen reduction of tungsten hexafluoride at various temperatures and pressures. It was shown that the growth rate at a given temperature displayed a square root dependence on changes in either the total pressure or the hydrogen partial pressure and no dependence on changes in the $WF_6$ partial pressure [5,7,49,50]. The activation energy was found to be 69,000 J/mol (0.71eV) on both a Si substrate [5] and a W substrate [49].

The characterization of a deposited film requires the use of a variety of diagnostic techniques. Modern surface science and other techniques provide the capability of studying metal films designed for use in microelectronics. These techniques allow the researcher to investigate such things as the uniformity and purity throughout films, the

porosity of a deposited film, and the condition of the interface after the deposition of a metal on a surface. This film morphology is greatly affected by the deposition parameters and the rate of deposition.

A few studies have been reported on the film morphology and chemical composition of the hydrogen-reduced W films. There exist at the tungsten/silicon interface a number of morphological features which occur on a submicron to atomic level. Paine et al. [9] reported the common features such as the formation of wormholes in the silicon substrate, tungsten/silicon interfacial roughness, and lateral encroachment of tungsten beneath silicon/silicon dioxide interfaces. It was also emphasized that the physical properties of the initial 10 nm of tungsten would play a role in interface morphology development.

In a study by Shroff and Delval [14], tungsten was deposited from the vapor phase by the reduction of $WF_6$ by hydrogen on various substrates such as copper, stainless steel, and molybdenum. The deposition temperature ranged from 450-1200$^O$C. The reaction was carried out at partial pressures of 5-760 torr; and the hydrogen to hexafluoride ratio was varied from 1 to 60. Their structural study of the deposits with optical and scanning microscopes showed that the number of very small voids or bubbles in the

deposits tended to increase with increasing $H_2/WF_6$ ratio and pressure, and decreased with increasing deposition temperature. The amount of gaseous fluorine impurity measured by the activation process, showed that the higher the ratio, the higher was the percentage of samples with low F content.

The characterization study of CVD W by MacLaury et al. [51] was performed at 300°C with a 30/1 $H_2/WF_6$ flow ratio at 0.3 torr. In the study it was found from SIMS(Secondary Ion Mass Spectrometer) analysis that fluorine was a major contaminant. The transmission electron microscopy (TEM) results indicated that some kind of damage to the (100) $Si/SiO_2$ interface in the form of worm tracks in the silicon under the $SiO_2$ step. The transmission electron micrographs published by Stacy et al. [52] support the fact that during the tungsten deposition filaments (variously called "wormholes" or "tunnels") were formed in the silicon substrate. However, filament growth was not observed onto aluminum but onto silicon. These observations led Stacy et al. [52] to conclude that the vaporization of silicon by fluorinated species was involved.

## Scanning Electron Microscopy (SEM)

The morphology of the Mo films deposited can be determined by scanning electron microscopy, which has become an important tool for VLSI analysis because it has the capability of providing much higher magnification, resolution, and depth of field than optical microscopy [53]. That is, the resolution of SEM can be up to 1nm (100nm is routinely obtained), the magnification from 10X-100,000X and the depth of fields of 2-4 μm at 10,000X. Especially, the high depth of field makes SEM useful for high magnification (i.e. >2,000X) examination of film thickness below 1 μm [54]. SEM analysis yields information on linewidth, film thickness, step coverage, interface roughness, and other morphological data.

In the scanning electron microscopy, an electron gun, usually consisting of tungsten or $LaB_6$, is used to create a beam of electrons that is accelerated to energies of 500eV-40keV, focused to a small diameter, and rastered across the sample surface. The electrons striking the surface produce three useful types of radiation: x-rays, secondary electrons, and backscattered electrons. A large fraction of the electron spectrum (usually below 50eV) are secondary electrons, which are produced by inelastic collisions of the primary beam and the inner shell electrons of the sample

atoms. Because they posses such low energies, only secondary electrons created close to the surface actually escape and are detected. The detected electron current, which can be due to secondary or backscattered electrons, but is typically the former, is used to modulate the intensity of an electron beam in a cathode ray tube (CRT). The CRT beam produces an image of the sample surface whose contrast is determined by variations in the secondary or backscattered electron flux [55].

## Auger Electron Spectroscopy (AES)

Auger electron spectroscopy has emerged as one of the most important techniques for determining the elemental composition of CVD films qualitatively and quantitatively. The utility and popularity of AES is based on its high sensitivity, its excellent elemental selectivity for all atoms except H and He, the availability of energy analyzers with high transmission, and the good lateral resolution afforded by electron beam excitation.

This technique is based on the fact that each element of the periodic table will, when excited by the ionization of a core level, emit Auger electrons at characteristic energies that are usually only slightly influenced by chemical environment. In the precursor process to the

Auger emission the initial core hole is produced by electron impact ionization in which the atom undergoes the transmission

$$A \longrightarrow A^+(i) + e^-$$
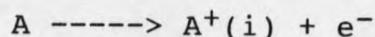
Here the notation $A^+(i)$ indicates that the hole in A is in level i. The Auger process may then be written

$$A^+(i) \longrightarrow A^{2+}(j,k) + e^-$$
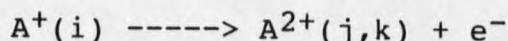
where the emitted electron $e^-$ has kinetic energy $E_k$ outside the solid; that is, it lies at a level $E_k + \Gamma_s$ above the Fermi level, and the atom is left doubly ionized with holes in its j and k levels. This process may be understood as involving an electron from an outer level j (or k), which is ejected. This simple explanation, however, neglects final-state interactions.

AES can be used to conduct a depth profiling of the deposited molybdenum. By combining continuous sputter etching with AES, the composition as a function of depth into the surface can be determined. This method has been extensively applied to a variety of technologically important problems in semiconductor, metallurgy, and thin-film processing [56]. A difficulty from this technique comes from the case in which quantitative data is needed. In that case, usually a standard is also required. That is, a sample containing a known quantity of the substance

whose presence is being quantitatively identified (determined with confidence by an alternate diagnostic technique), must be analyzed to establish reference signal magnitudes for the characterization technique being used. In fact, all compositional analysis techniques except Rutherford backscattering (RBS) require such standards as a prerequisite to obtaining accurate quantitative data.

# RESEARCH OBJECTIVES

The objectives of this study are basically two-fold:

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

2. Characterize the silicon-reduced Mo films by AES, SEM, and and compare the findings with those reported in the literature.

## EXPERIMENTAL EQUIPMENT

The reactor for LPCVD Mo used in this study was drawn in Figure 1, which was divided by function into the following primary components: the gas flow controller, the reactor and heater, the chamber pressure controller, the pumps, and the after-burner and alumina trap.

### Gas Flow Controller

Electronic E-1 grade pure helium (99.9995%, Scientific gas products inc.) and molybdenum hexafluoride (99.9% pure, SERAC Co.) were introduced into the reaction chamber by MKS type 1259 controllers, which were connected to a MKS 247B four channel readout and power supply unit.   The flow rates of both He and $MoF_6$ gases could be set at 3 and 9 sccm, respectively.   The controllable gas flow ranges were 0-145 sccm for helium and 0-21 sccm for molybdenum hexafluoride.

### Reactor and Heater

The 6 way-cross stainless steel reaction chamber was wrapped with fiberglass heating tape to reduce water vapor inside the reactor.   The substrate heater was mounted on the stainless steel rod attached to a flange.   A 5cm x