



Kinetics of the tungsten hexafluoride-silane reaction for the chemical vapor deposition of tungsten
by Huseyin Gokce

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemical Engineering
Montana State University
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Abstract:

Tungsten has been used for multilevel metallization in very large scale integration (VLSI) technology. Reduction by silane has been considered as a high-rate, low-temperature process alternative to hydrogen reduction of tungsten hexafluoride in the chemical vapor deposition of W. In the present study, the kinetics of the low pressure chemical vapor deposition (LPCVD) of tungsten by silane reduction of tungsten hexafluoride on Si(100) surfaces was studied.

A single-wafer, cold-wall reactor was used for the experiments. The SiH₄/WF₆ ratio was 1.0. The pressure and temperature range were 1-10 torr and 137-385°C, respectively. Kinetic data were obtained in the absence of mass transfer effects. The film thicknesses were measured by gravimetry. Scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray diffraction (XRD), and resistivity measurements were used to analyze the W films.

For the horizontal substrate position and 4-minute reaction times, the apparent activation energies were determined to be 0.35 eV/atom for 10 torr, 0.17 eV/atom for 3 torr, and 0.08 eV/atom for 1 torr. Lower temperatures and higher pressures produced porous films, while higher temperatures and lower pressures resulted in continuous films with smoother surfaces. At the Si-W interface, a W(110) preferential orientation was observed. As the W films grew thicker, W orientation switched from (110) to (100). Apparent activation energy seems to change with thickness.

Si and F contents of the films were within the noise level for Auger detection. Porosity was found to be influential in the film resistivity.

The higher activation energy observed at higher pressure was deduced to be a result of limitations in the rate of SiH₄ adsorption and subsequent adatom surface diffusion. The domination of W(100) orientation for thick films at high temperatures was attributed to a reconstruction of W(100) surfaces on which adatom surface diffusion is easier.

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APPROVAL

of a thesis submitted by

Huseyin Gokce

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Dedicated to my parents,
Habibe and Emin Gokce

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ABSTRACT

Tungsten has been used for multilevel metallization in very large scale integration (VLSI) technology. Reduction by silane has been considered as a high-rate, low-temperature process alternative to hydrogen reduction of tungsten hexafluoride in the chemical vapor deposition of W. In the present study, the kinetics of the low pressure chemical vapor deposition (LPCVD) of tungsten by silane reduction of tungsten hexafluoride on Si(100) surfaces was studied.

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For the horizontal substrate position and 4-minute reaction times, the apparent activation energies were determined to be 0.35 eV/atom for 10 torr, 0.17 eV/atom for 3 torr, and 0.08 eV/atom for 1 torr. Lower temperatures and higher pressures produced porous films, while higher temperatures and lower pressures resulted in continuous films with smoother surfaces. At the Si-W interface, a W(110) preferential orientation was observed. As the W films grew thicker, W orientation switched from (110) to (100). Apparent activation energy seems to change with thickness.

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CHAPTER 1

INTRODUCTION

In the mid 1970's, very large scale integration (VLSI) technology started with 64Kbit dynamic random access memory for dynamic memory devices and specific integrated circuits. The technology has recently improved to provide 16Mbit capacities. It is predicted that at the end of the 20th century, dynamic memory chips will reach 1 gigabit capacity [1]. This much memory is only one-tenth of the number of neurons in a human brain. Thus, one memory board would be equivalent to a human brain in terms of data storage.

The developments in the VLSI technology have been making ultra-large scale integration (ULSI) technology a coming reality, as submicron dimensions can be utilized. Such a transmutation in the technology has certain requirements. Some of them include high aspect via-contacts, complicated geometry in multi-level interconnections, high current density, and shallow junctions at source/drain regions. These requirements have directed the researchers to look for new materials which can provide low contact resistance, smooth interconnections to prevent electromigration, and low temperature processibility.

It has been shown that selectively deposited tungsten (1,000 - 1,500 Å) on monosilicon or polysilicon surfaces in metal-oxide silicon (MOS) device structures can serve as an

interconnect shunt and contact diffusion barrier [2]. The term "selective deposition" is used when tungsten (W) is deposited only onto silicon (Si) and surrounding silicon dioxide (SiO_2) is free of deposition.

Tungsten hexafluoride, a commonly used source gas for tungsten deposition, can be reduced by either silane, hydrogen or silicon substrate itself. The kinetics for tungsten deposition by Si and H_2 reduction of WF_6 has been studied extensively and the parameters have been well established [3-6]. The Si reduction reaction causes the consumption of the silicon substrate and produces very rough W-Si interfaces. The deposition reaction stops after a limiting W film thickness is reached ($\sim 300 - 400 \text{ \AA}$). H_2 reduction reaction does not show a self-limiting behavior but has some drawbacks, such as silicon consumption of the substrate which appears in the form of tunnels and required high deposition temperatures for practical deposition rates.

Chemical vapor deposition (CVD) of tungsten by hydrogen (H_2) reduction of tungsten hexafluoride (WF_6) is considered to be a potential technique for integrated-circuit applications. Low pressure chemical vapor deposition (LPCVD) has some proven advantages over atmospheric pressure CVD. These advantages are increased control over the deposition ambient, greater throughput, lower reactant gas flows, high purity deposits, and excellent deposit uniformities and conformities.

Silane (SiH_4) reduction of WF_6 was shown to suppress silicon consumption and tunneling [7,8]. Therefore, the leakage current and contact resistance is low, which are the desired electrical properties. Kinetic studies on the LPCVD of tungsten using SiH_4 - WF_6 reaction system have been very limited since most studies aimed at developing a better tungsten film quality rather than establishing the kinetic parameters [7-10]. All the researchers have observed a complicated behavior in the temperature dependence of the kinetics of the SiH_4 - WF_6 reaction, and thus, no Arrhenius activation energies have been reported.

Research Objective

An efficient design for a commercial production system requires knowledge of reaction kinetic parameters. The lack of kinetic parameters for the SiH_4 - WF_6 system is the motivation for this study. The research objectives are:

- (1) To measure and evaluate kinetic data for the chemical vapor deposition of tungsten by SiH_4 reduction of WF_6 . The substrate surface is to be Si(100) and the kinetic data will be acquired under differential reactor conditions. The deposition rates will be determined by a gravimetric method.
- (2) To examine the quality of the tungsten films deposited by the WF_6 - SiH_4 reaction. Thin W films will be analyzed with

scanning electron microscopy (SEM), x-ray diffraction (XRD), Auger electron spectroscopy (AES), and resistivity measurements.

- (3) To interpret the kinetic data in the context of the morphology and crystal structure studies. Parameters are the reaction temperature and pressure, the gas flow rate, the film morphology, and the crystal orientation.

CHAPTER 2

LITERATURE SURVEY

Thin Films

VLSI devices use a variety of thin films as metals, semiconductors, and insulators. A better understanding of chemical and physical properties of thin films is essential to improve the device performance. There are specific methods developed to form thin films for different applications [11]. Regardless of the method of formation, VLSI fabrication requires that the process be economical and the resultant film have the following properties [12]:

- Good thickness uniformity.
- High purity and high density to provide good insulation (or conduction) and integrity.
- Controlled composition and stoichiometries.
- High degree of structural perfection to ensure film continuity over the lifetime of the device.
- Good electrical properties.
- Excellent adhesion and low stress values to eschew film discontinuity due to deformation, cracking, undercutting, and lifting effects.
- Good step coverage.

It is known that the properties of a thin film may be quite different from those of the bulk material. These differences are more pronounced as the film thickness gets extremely small, namely at the micron level. For one thing, thin films have a higher surface-to-volume ratio than a bulk material which makes the surface properties more influential on the film properties. For another, the peculiar structure of the thin film is an important factor in determining the film properties, and this structure is dictated by the nature of the processes which occur during film formation.

Thin Film Formation

Thin films can be formed by a large variety of techniques [13]. In VLSI fabrication, the formation of thin films can be categorized into two major procedures:

- (1) Film growth by interaction of a vapor-deposited species with the substrate.
- (2) Film formation without causing changes to the substrate.

The first category includes thermal oxidation and nitridation of single crystal silicon and polysilicon substrates, and the formation of silicides by direct reaction of a predeposited metal and the substrate.

The second category includes three forms of deposition on the substrate:

i) Chemical vapor deposition (CVD), where solid films are deposited on a substrate by reacting vapor phase chemicals on the substrate surface. Amorphous, polycrystalline and single-crystalline films can be formed by CVD. The process is called epitaxy when CVD is used to form single-crystal thin films.

ii) Physical vapor deposition (PVD), where the atoms of the material to be deposited are physically dislodged from a source material into vacuum, then the condensation occurs on the substrate to form the thin film. PVD processes include evaporation, sputtering and molecular beam epitaxy.

iii) The deposition of a liquid on a substrate which is then dried to form the solid thin film. Spin-coating is the most commonly used technique.

Thin film deposition by most common processes, such as PVD and CVD, involves a condensation transformation from the vapor to the solid phase. The formation of a thin film can be best understood by the thermodynamic and kinetic analysis of the condensation phenomena [14,15].

Condensation and Nucleation

The initial step of thin film nucleation in CVD and PVD is the impingement of vapor molecules onto the substrate. After impingement, the vapor molecules can either adsorb and stick permanently to the substrate, or they adsorb momentarily and re-evaporate, or they ricochet back to the vapor phase.

The initial attraction of the impinging atom (or molecule) requires that instantaneous dipole or quadrupole moments of the surface atoms exist. The excess energy of the attracted atom is transferred to the substrate in the form of lattice oscillations. The attracted atom then becomes attached to the surface after losing its velocity component normal to the surface. The attachment of impinging vapor atoms on the surface is known as "adsorption" and the adsorbed atom is called "adatom".

Two types of adsorption phenomena have been recognized in principle:

i) Physisorption caused by secondary (van der Waals) attractive forces.

ii) Chemisorption caused by chemical bonding involving transfer of electrons between adsorbent and adsorbate.

Because of the nature of the bonding involved, physisorption is associated with much smaller binding energies (~ 0.25 eV) than is chemisorption (8-10 eV).

Adsorbent surfaces may be pictured as an array of adsorption sites where each adsorbed molecule occupies a minimum potential energy site [16]. An adsorbed atom may retain its initial lateral momentum or may be activated thermally from the surface so that it will jump over the energy barriers into the next available adsorption site. It is also possible that some of the adatoms re-evaporate from the surface into the vapor phase. The factors that affect the

rates of adsorption and desorption (re-evaporation) are given by the functions below, in which the variables are assumed separable. Then rate of adsorption, μ_a , is [17]

$$\mu_a = \frac{P}{\sqrt{2\pi mkT}} \sum_{i=1}^m n_i \sigma_i f(\theta_i) e^{-E_i/RT} \quad (1)$$

and rate of desorption, μ_d , is

$$\mu_d = \sum_{i=1}^m n_i K_i f'(\theta_i) e^{-E'_i/RT} \quad (2)$$

where,

m : number of types of sites.

n_i : number of sites of type (i).

θ : surface coverage.

$f(\theta)$, $f'(\theta)$: function for the surface coverage dependence of adsorption and desorption, respectively.

R : gas constant.

E , E' : activation energy of adsorption and desorption, respectively.

σ , K : condensation and evaporation probability, respectively.

$P/(2\pi mkT)^{0.5}$: number of collisions with a surface

(m : mass of atom, k : Boltzmann constant).

Equations 1 and 2 indicate that adsorption rate is a function of both pressure, P , and temperature, T , while desorption rate is not influenced by pressure, but by temperature.

As the adatoms migrate along the surface, they collide with other atoms and form clusters of adsorbed atoms. The

small clusters consist of only a few atoms and have very high surface-to-volume ratios. This results in high surface energy values and energetically unstable clusters which have a high tendency to re-evaporate. For this reason, most theories on condensation and nucleation define a critical radius for clusters above which the total free energy of the system decreases with increasing radius. Hence, clusters larger than this critical size are stable and favor a continued growth. The stable clusters are called "nuclei" and the mechanism of their formation is termed "nucleation".

There are two basic models to explain the nucleation phenomena: the capillarity model which employs simple idealized geometrical shapes for the cluster [18,19], and the atomistic (or statistical) model [20] which uses only discrete arrangements of atoms. Furthermore, the capillarity model predicts a continuous variation of crystal size and nucleation rate with the degree of supersaturation, whereas the atomistic model predicts discontinuous changes which are more pronounced for smaller critical cluster sizes. In the limit of large critical nuclei, the two models become identical.

In the initial stages of condensation, clusters of various sizes are in metastable equilibrium with free adatoms. As the clusters grow to supercritical dimensions, they deplete the adatoms within their surrounding regions in which any further cluster formation (or nucleation) is not possible. These regions are called "capture zones".

It is observed that the film mass deposited depends on the total impingement time, the substrate temperature, the diffusion coefficient of adatoms on the surface, the mean residence time of adatoms, and the impingement rate [21]. The "onset" of condensation is defined by the initial formation of nuclei and is marked experimentally by the appearance of some observable mass of condensate on the substrate. The corresponding substrate temperature is called the "critical" condensation temperature. The critical temperature, T_c , however, depends on the observation time. If the adatoms have long enough mean free residence times of adherence on the surface at temperature T_c , all impinged atoms will be captured by stable nuclei so that the sticking coefficient will be unity even initially. For temperatures greater than T_c , the adatoms have less residence time on the surface due to increased desorption from the surface, therefore longer times are required for the onset of condensation.

Lewis and Campbell [22] have analyzed the nucleation process near T_0 for the case of the smallest possible critical nucleus. Figure 1 shows how the saturation density of nuclei changes with temperature and identifies incomplete and complete condensation temperature regions. At low temperatures or high impingement rates (complete condensation), the

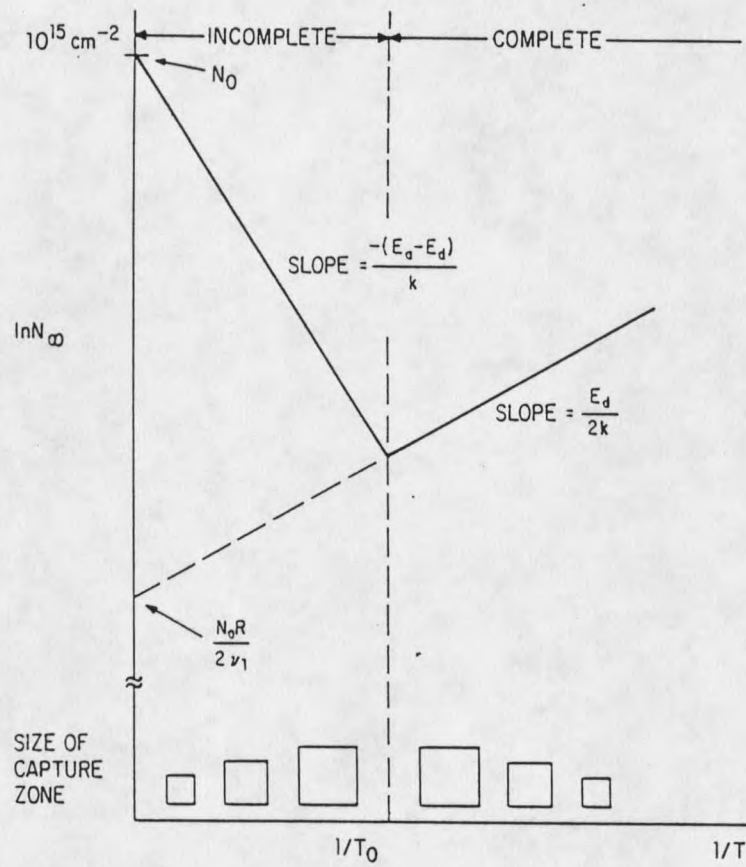


Figure 1. Saturation density of nuclei vs. reciprocal temperature, illustrating the boundary between initially complete and incomplete condensation [22].

impinged atoms immediately form stable pairs of density N_0 without the possibility of re-evaporation. In this region, the slope of the $\ln N_0$ vs. $1/T$ plot is positive since the diffusion coefficient increases with increasing temperature, hence increasing the size of the capture zone where further nucleation is not possible. At high temperatures (incomplete condensation), the slope is negative because increased temperatures lead to re-evaporation of adatoms which means smaller mean residence times. The result is decreased size of the capture zone around each nucleus, yielding more nuclei on the substrate.

Zinsmeister [23] has claimed that the desorption and evaporation of clusters, as well as adatoms, are not negligible in spite of the much greater activation energy involved. He indicated that at the beginning of the condensation, adatoms and very small clusters predominate, but later most of the condensate is tied up in larger clusters. He also showed that the sticking coefficient is low at the beginning of the condensation.

Film Growth

Electron-microscopic studies have revealed the different stages of film growth. Pashley, et al. [24] have identified the four basic stages of the growth process, namely, nucleation and island structure, coalescence of islands,

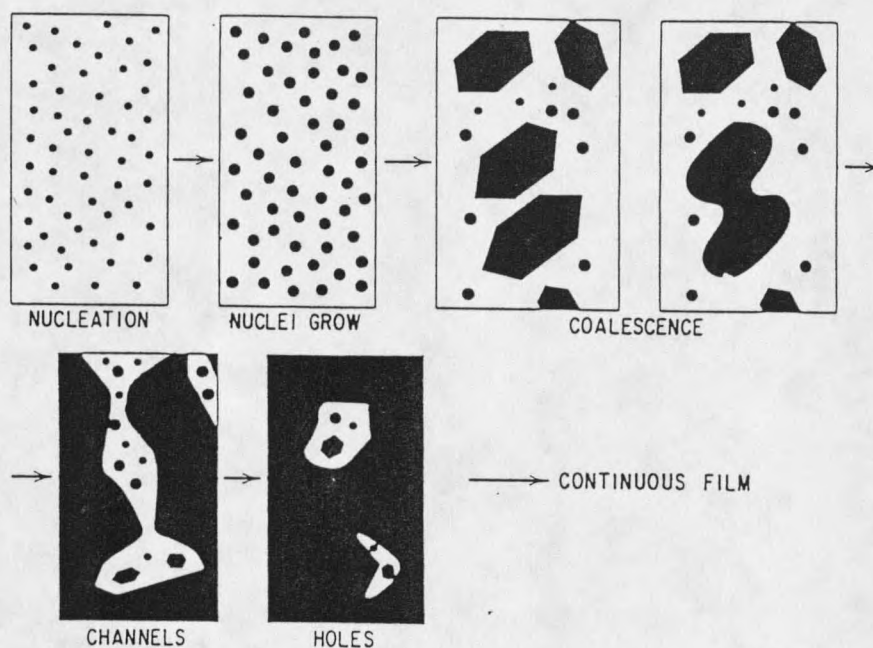
channel formation, and the formation of the continuous film. These stages are shown in Figure 2a and 2b and explained in the following sections [14].

(1) The Island Stage: Upon the onset of condensation, the initial nuclei are fairly uniform in size. Although the growth is three-dimensional in nature, the growth parallel to the substrate is greater than that normal to it. This implies growth as a result of surface diffusion of adatoms rather than growth by direct impingement.

(2) The Coalescence Stage: As two neighbor nuclei grow, at some point they touch each other and a liquid-like coalescence occurs as shown in Figure 2b. The driving force for coalescence is the reduction of surface energy by the formation of a new composite island which has a smaller surface-to-volume ratio.

A triangular, straight edged shape of the crystallites is characteristic of the late nucleation stage (Figure 2a). During coalescence, these well-defined crystallographic shapes become rounded. Mass transfer may occur by both volume and surface diffusion, but surface diffusion is shown to be the predominant mode. Curvature differences on the surface of the coalescing islands create surface tension forces, which drive atoms on the surface from convex-shaped regions to concave-shaped regions. These forces

(a)



(b)

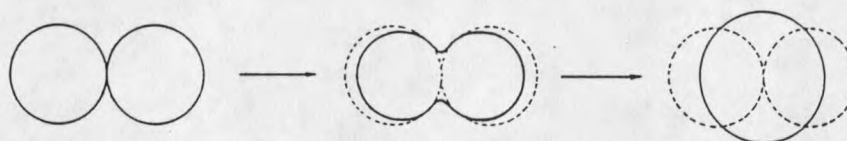


Figure 2. (a) Schematic of the stages of film growth.
 (b) Schematic of the shape changes during coalescence [24].

are minimized at the end by the formation of a rounded island. As a result, a reduction in area and an increase in height occur which, in turn, reduce the total substrate area covered by the islands.

In addition to surface area reduction, the surface energy is also reduced by rearranging the crystal orientation. After coalescence, preferred boundary planes are observed and the composite island assumes a hexagonal shape.

(3) The Channel Stage: During each coalescence, the smaller nuclei are pulled into more massive regions of the film leaving fresh substrate area for further secondary nucleation. As the islands grow and coalescence takes place continually, the islands become elongated and form larger islands separated by long channels or holes. The channels contain many secondary nuclei, which coalesce with each other and with the main film, thus increasing the main film mass and leaving fresh substrate areas behind for further secondary nucleation. Each repetition of this process makes the channel smaller and the cycle continues until the channel is filled in.

(4) The Continuous Film: Pashley et al. [24] observed that during film growth, especially in the coalescence stage, island orientation changes by recrystallization. A considerable degree of recrystallization occurs even at room

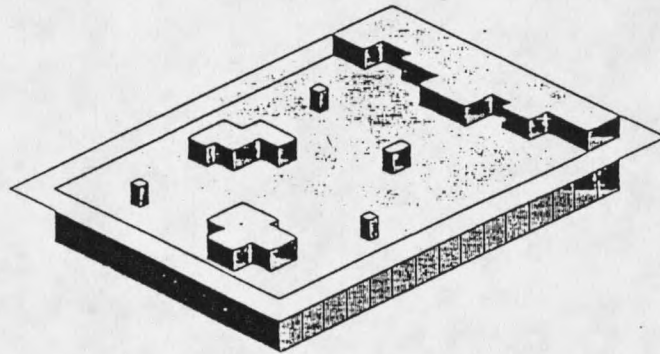
temperature. Each grain in a polycrystalline film incorporates a very large number of initial nuclei. Thus, the resulting number of crystals in a continuous film is significantly less than the initial number of nuclei.

Growth Modes

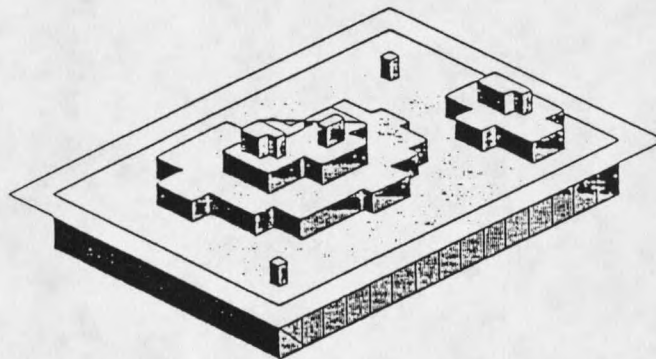
Three basic growth modes are recognized and named after the authors who established them: the Frank-van der Merwe (FM), the Stranski-Krastanov (SK), and Volmer-Weber (VW) modes [25]. These modes are illustrated in Figure 3. Bauer [26,27] has demonstrated that relative surface energies dictate the growth mode. Neglecting edge energies and the shape and size dependence of the surface energies, the equation governing the growth mode is

$$\Delta = \sigma_f + \sigma_i - \sigma_s \quad (3)$$

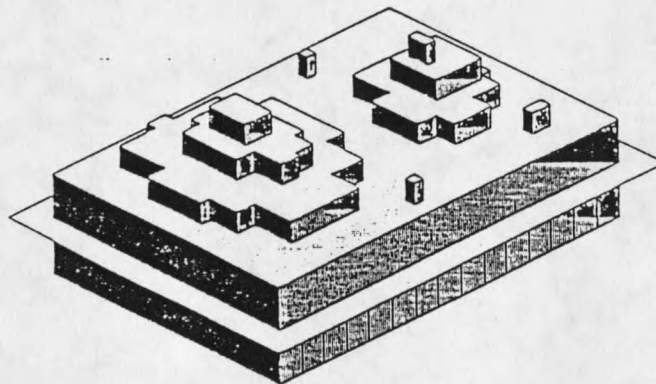
where, σ_f and σ_s are the specific free surface energies of film and substrate, respectively, and σ_i is the specific free interfacial energy. If the deposited material has a higher surface energy than the substrate ($\Delta > 0$), the film will tend to form a three-dimensional structure (VW mode), otherwise a layer by layer growth (FM mode) is favored ($\Delta \leq 0$). When σ_i changes with the size and shape of the island as the layers grow, transitions between the two modes occur and 3-D crystals grow on top of one or a few monolayers (SK mode).



(a)



(b)



(c)

Figure 3. Various modes of growth of an overlayer on a substrate: (a) Frank-van der Merwe, (b) Volmer-Weber, and (c) Stranski-Krastanov growth. The horizontal plane indicates where the substrate ends [25].

Epitaxial Growth

Epitaxy: from the Greek, $\epsilon\pi\iota$ (epi: placed or resting upon) + $\tau\alpha\chi\iota\zeta$ (taxis: arrangement). Epitaxy = "the growth of crystals on a crystalline substrate that determines their orientation" [25].

Frankemheim [28] pioneered the science of epitaxy by demonstrating that sodium nitrate can be grown from a solution onto a calcite crystal with a unique orientation relationship. Royer [29] used x-ray diffraction (XRD) to show that such oriented growth requires that lattice planes in both materials have similar structure and orientation to the substrate material; he concluded that epitaxial growth requires a lattice misfit of not more than about 15%. Lattice misfit, ϵ , is defined by

$$\epsilon = \frac{b - a}{a} \quad (4)$$

where, a and b are the in-plane lattice constants of substrate and overgrowth, respectively. Thus the occurrence of epitaxial growth is probable whenever the substrate and overgrowth have coincident lattices and low interfacial energy. Lattice mismatch causes a strain at the substrate-overgrowth interface. This strain is relieved by creating misfit dislocations in the overgrowth at the interface. Studies have been carried out to identify and characterize misfit dislocations at epitaxial interfaces [27,30].

Thin Film Analysis Techniques

X-ray Diffraction

As a crystallographic analysis method, x-ray diffraction is used for determining substrate orientation, for characterizing crystalline phases and preferred orientations in crystalline layers, and for identifying amorphous regions [31].

X-ray diffraction utilizes the following geometrical arrangements as illustrated in Figure 4:

- (1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always on the same plane.
- (2) The angle between the diffracted beam and the transmitted beam is 2θ .

Diffraction occurs when the wavelength of the incident beam matches with the repeat distance between scattering centers to form a constructive interference. The criterion to be met for the Bragg law is

$$n\lambda = 2d\sin\theta \quad (5)$$

where, λ is the x-ray wavelength, d is the interplanar spacing, θ is the Bragg diffraction angle, and n is an integer giving the order of the diffraction. This geometry is illustrated in Figure 4. The experimentally measured angle is usually the diffraction angle, 2θ , rather than θ .

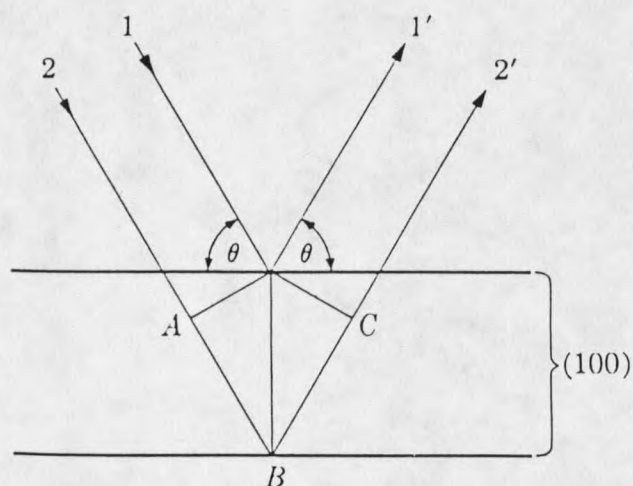


Figure 4. Equivalence of a second order reflection [31].

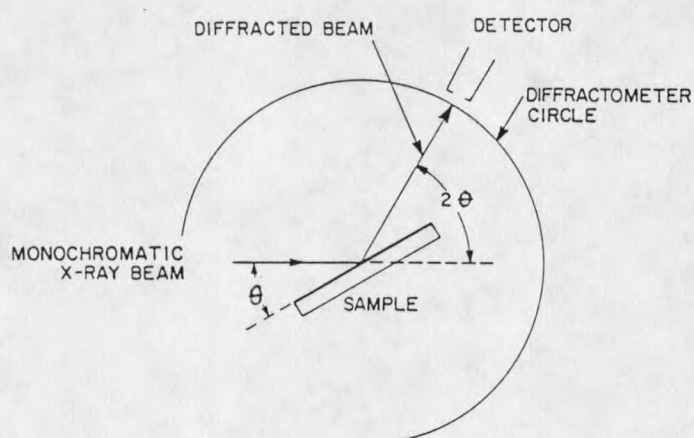


Figure 5. X-ray diffractometer configuration. As the sample rotates over an angle θ the detector moves along a circumference an angular distance 2θ ; a diffraction maximum occurs when θ is equivalent to a Bragg angle [32].

Four types of x-ray diffraction are commonly employed in VLSI fabrication processes; the Laue technique, the Read camera technique, the Huber-Seemann-Bohlin, and diffractometer methods. All these methods are based on establishing conditions that satisfy the Bragg requirement. More precise measurements of lattice parameters are obtained using a diffractometer geometry [32].

Diffractometer Method: The x-ray spectrometer is called a diffractometer when it is used with x-rays of known wavelength to determine the unknown spacing of crystal planes [31]. As a spectrometer, it is used to determine unknown wavelengths from crystal planes of known spacing. A diffractometer is shown in Figure 5 [32]. A monochromatic x-ray beam strikes the film surface at an angle θ . As the sample is slowly rotated, the detector is also rotated along the circumference of a circle with the same center as the sample. The detector moves in concert with the sample to maintain the diffraction angle, 2θ , at all times. Diffraction peaks appear wherever θ coincides with a Bragg angle. Data are usually recorded on a strip chart recorder as diffraction intensity, I , versus diffraction angle, 2θ . Then, the obtained diffraction pattern is matched with the patterns recorded in the ASTM Powder Diffraction Data File [33] for identification of the crystal structure.

Sheet Resistance

Sheet resistance values are used to electrically characterize the thin films in silicon microcircuits [34]. Consider a rectangle of a layer of length ℓ , width b , and thickness t as shown in Figure 6 [35]. The resistance measured in the direction parallel to the film is

$$R_s = \rho \frac{\ell}{bt} \quad (6)$$

where, ρ the resistivity of the film. If ℓ and b are sufficiently large or equal to each other, Equation (6) becomes

$$R_s = \frac{\rho}{t} \quad (7)$$

and is defined as sheet resistance of the film in ohm/square ($\Omega/\square$). R_s is then independent of the size of the square but dependent on the film resistivity and film thickness. When the thickness and sheet resistance are measured, the film resistivity can be calculated by

$$\rho = R_s t. \quad (8)$$

Four-point Probe Method: Among the several techniques for measuring sheet resistance, the four-point probe method is widely used [36]. Figure 7 schematically shows a four-point probe measuring set-up. The probes are placed colinearly, with an equal spacing of a . A reference current I is forced between the outer two probes and the resulting voltage drop V is

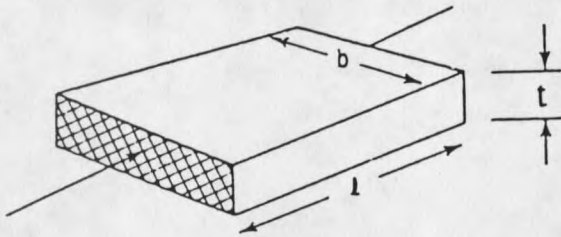


Figure 6. Definition of sheet resistance [35].

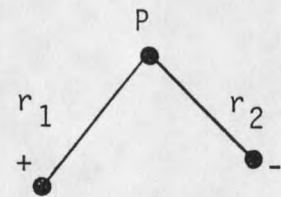


Figure 8. Positive and negative sources relative to point P.

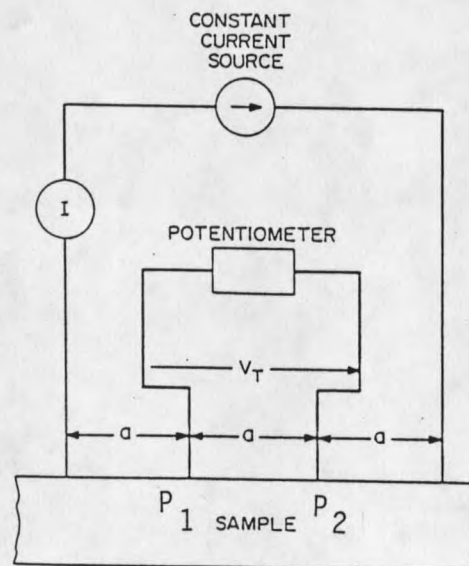


Figure 7. Schematic diagram for a four-point probe measuring setup.

measured between the inner probes. Consider a configuration in Figure 8. Point P is located at a distance r_1 to positive the source of current. If the layer has infinite dimensions, the potential, ψ , at point P is given by

$$\psi = \frac{IR_s}{2\pi} \ln \frac{r_2}{r_1} + A \quad (9)$$

where A is a constant of integration and I is the current. In the case of a four-point probe configuration (Figure 7) the potentials, ψ_1 and ψ_2 at points P_1 and P_2 can be expressed as

$$\psi_1 = \frac{IR_s}{2\pi} \ln 2 + A \quad (10)$$

and

$$\psi_2 = \frac{-IR_s}{2\pi} \ln 2 + A \quad (11)$$

Then, the resulting potential difference between P_1 and P_2 can be calculated by

$$\psi_1 - \psi_2 = V = \frac{IR_s}{\pi} \ln 2 \quad (12)$$

Thus, the sheet resistance is

$$R_s = \left(\frac{\pi}{\ln 2} \right) \frac{V}{I} \quad (13)$$

and

$$R_s = 4.5324 \frac{V}{I} \quad (14)$$

Hence, for an infinite sheet, the sheet resistance can be directly calculated from the V/I ratio. For the samples with finite dimensions Equation 14 can be generalized as

$$R_s = C \frac{V}{I} \quad (15)$$

where C is a correction factor and is a function of the probe spacing and sheet dimensions [37].

Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a standard analysis tool in VLSI laboratories because of its superiority over optical microscopy [38,39]. A magnification of 100,000X with a spatial resolution better than 100 Å can be obtained with SEM, whereas for optical microscopes, these figures are 1,000X and 10,000 Å, respectively. SEM can give a depth of field of 2-4 μm at 10,000X magnification and 0.2-0.4 mm at 100X magnification which are much deeper than those of optical microscopes. Thus, SEM provides information on line width, film thickness, step coverage, edge profiles after etch, and other morphology data for VLSI device surfaces.

In an analogous manner to light, when an electron interacts with a specimen, the electron can be partially or completely transmitted, partially or completely absorbed, or scattered by reflection and refraction. Absorption may result in fluorescence, phosphorescence, heating of the specimen, the ejection of photoelectrons, or a combination of these. Figure 9 shows the energy distribution of electrons emitted from a surface bombarded by an electron beam of energy E_0 .

Three predominant electron emissions are observed.

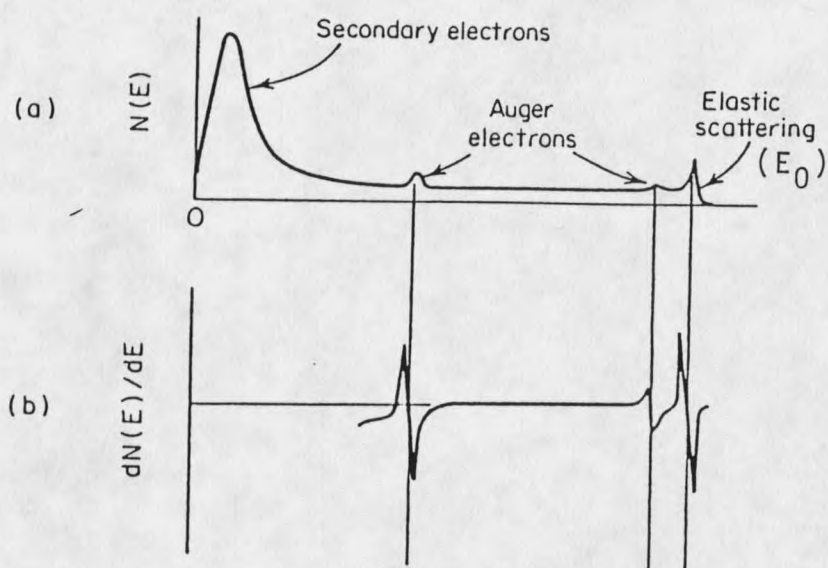


Figure 9. (a) Energy spectrum of electrons emitted from a surface bombarded by an electron beam. (b) The derivative of the number of emitted electrons with respect to the energy [38].

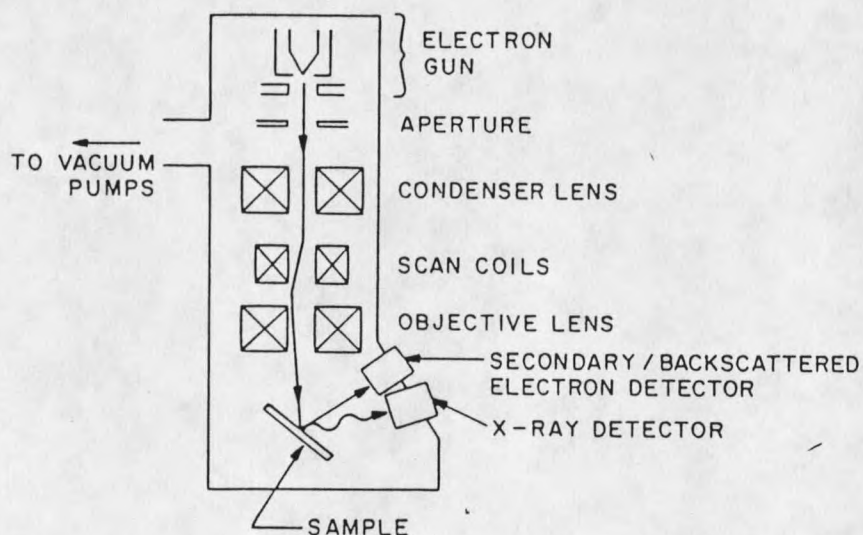


Figure 10. Schematic drawing of a scanning electron microscope [39].

- (1) Higher energy electrons. These electrons are backscattered and their energy is close to that of the primary beam.
- (2) Auger electrons. Peaks of these electrons occur between E_0 and 50 eV and they are discussed in detail in the Auger electron spectroscopy section.
- (3) Lower energy electrons. They generally have energies between 0 eV and 50 eV, peaking at less than 5 eV. These electrons are referred to as secondary electrons and are produced by inelastic collisions of the primary beam and the inner shell electrons of the sample atoms.

Because of their low energies, the only emitted secondary electrons are those which suffer the least inelastic scattering, and thus come from the atoms located very close to the surface. The escape depth of electrons in metals reaches a minimum of 4 Å at 70 eV, and increases with decreasing energy to a value of 25 Å at 10 eV. The escape depth is more than 50 Å for insulators. Because secondary electrons have a short escape depth, they exhibit better point-to-point resolution than do backscattered electrons. Mostly, secondary electron current rather than backscattered current is used to modulate the intensity of an electron beam in a cathode ray tube (CRT). The rastering incident beam of the SEM and the CRT

electron beam move synchronously across the sample surface to produce the image on the CRT screen.

A schematic diagram of an SEM is shown in Figure 10. The electron beam source can be tungsten hairpin, lanthanum hexaboride (LaB_6), field emission, and Schottky emitter sources which give different resolution and brightness levels.

The contrast of the image depends on the variations in the flux of electrons arriving at the detector [40]. Secondary electron yield is a strong function of the work function of the material, and is significantly higher for oxides and other wide-band gap materials than for silicon. The second source of contrast in secondary electron images is due to the dependence of secondary electron yield on surface curvature. The electron flux from a surface of changing slope varies with the secant of the tilt angle, thus making surfaces with different slopes easily distinguishable. The last source of the contrast is the orientation of the emitting surfaces with respect to the detector. Surface regions that face the detector appear brighter than other surface regions.

Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a quite commonly used electron spectroscopic technique [41,42]. The Auger electron emission process for silicon is shown in Figure 11 [43]. When an electron or photon strikes the surface of the sample, a primary electron is ejected from the K-shell of the

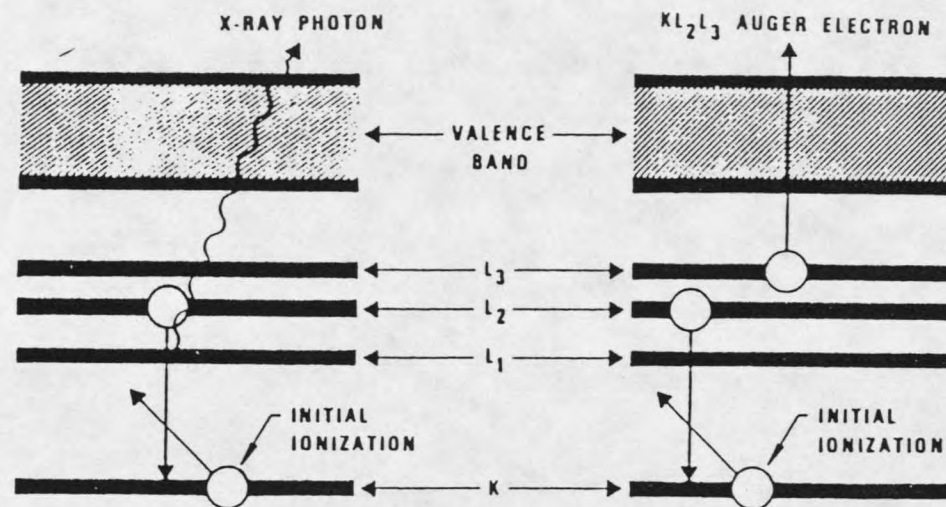


Figure 11. X-ray and Auger electron emission during de-excitation of atom after initial ionization [43].

atom leaving a hole in the core level of the system. An electron from the L-2 level relaxes into the K-shell to fill the empty position. During the relaxation process, a photon is emitted. This photon may either escape the material or interact with it. In the case of interaction it causes the ejection of a lower energy electron, such as L-3 level. This ejected electron is called an Auger electron and is labelled a KLL Auger electron in this case. Auger electrons are characteristic of the atom that emitted them. Since the Auger process requires the involvement of three electrons, H and He can not be detected with AES.

The incident electron beam energy is generally around 2-10 keV and can penetrate only a short distance into the sample. Most Auger electron energies are between 20 and 2,000 eV. Electron escape depth is defined as the distance from the surface across which the number of monoenergetic electrons emitted drops to 36.8% (e^{-1}) of their original value. The escape depth for Auger electrons is generally less than 50 Å. This enables one to perform a chemical analysis of surface regions from AES data.

It is shown in Figure 9a that Auger electrons constitute a small portion of the number of electrons emitted from a surface, therefore noise from other types of electrons is inevitable. Auger electron signals can be distinguished by performing a differentiation (dN/dE) using lock-in amplifiers

as shown in Figure 9b. An Auger spectrum of a W film surface on Si is given in Figure 12.

AES can detect elements above the concentration range of 0.1-1% at the sample surface. Quantitative information about the composition C_i of element i is obtained from the formula

$$C_i = \frac{\alpha_i I_i}{\sum \alpha_j I_j} \quad (16)$$

where, I_i is the intensity of the Auger peak of pure element i , and j indicates a summation over all the elements present in the matrix. The proportionality constant α is determined from known standards.

It is also possible to obtain compositional information about the material beyond the escape depth of Auger electrons. To achieve this, AES is combined with ion sputtering. During the AES analysis, ion sputtering is used for the continual creation of new surfaces through the sample. Data are then obtained by interrupting the sputtering at regular intervals and taking an Auger spectra. Hence, one can plot Auger peak heights as a function of sputtering time (or the equivalent depth) to obtain an AES depth profile. The incident electron beam size mostly determines the lateral resolution and is smaller than $0.1 \mu\text{m}$. Auger electron escape depth, on the other hand, determines the depth resolution and is about one monolayer for lower energy electrons.

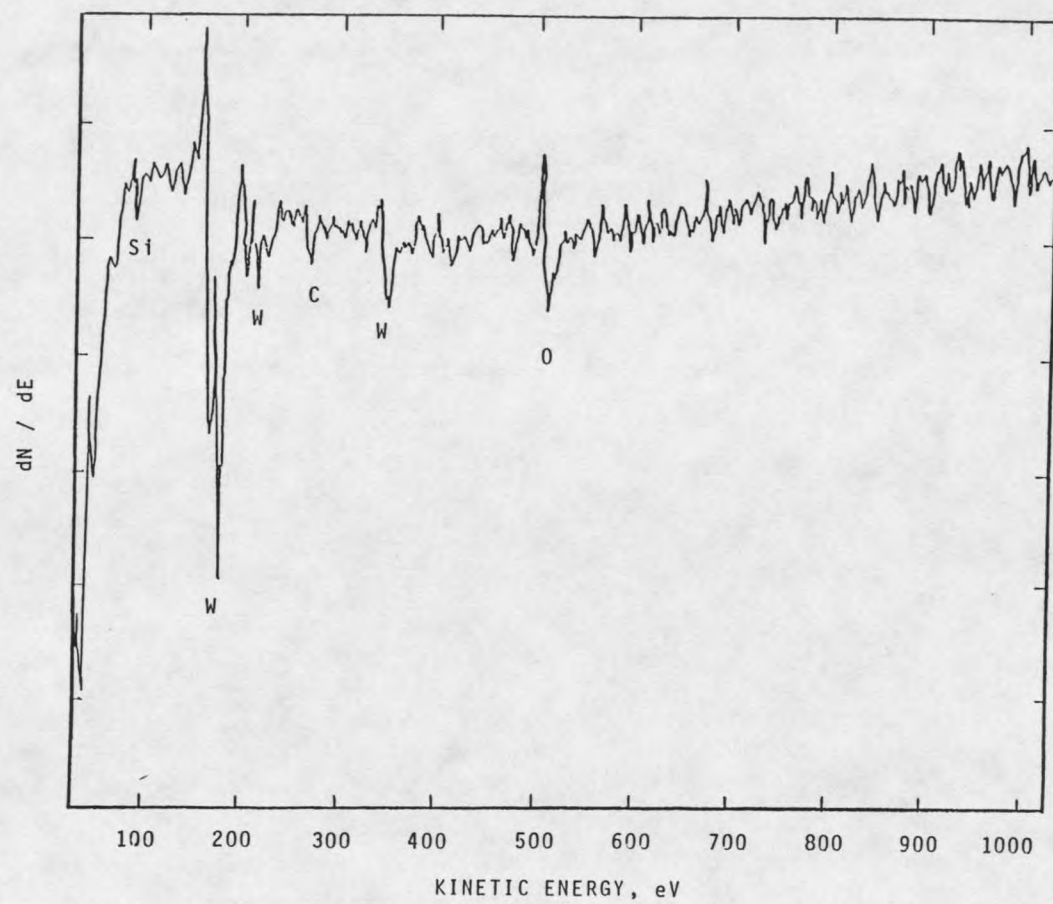


Figure 12. Auger spectrum of W film surface on Si.

Other important characteristics of AES are as follows: Upon exposure to an electron beam, samples of non-conducting nature have a propensity to charging. Thus, the analysis of insulators by AES is limited. A high energy incident electron beam can damage the surface under examination. Ion sputtering during depth profiling is a destructive method. Matrix effects can alter the signal position and intensity. Larger detection areas, longer scan times and narrower energy range scans increase the detection limit.

The common application of AES to VLSI technology includes the analysis of dopant and contaminant concentration in thin films and on surfaces, and determination of interface characteristics [43].

Film Thickness Measurement

Thickness of the deposited thin films is crucial in VLSI applications [44]. A thinner film introduces a higher resistance which can result in poor device performance. On the other hand, a thicker film will require longer etching times to reach the desired film thickness necessary for the application. Mostly, the thickness during physical evaporation is monitored with a resonator plate made from a quartz crystal. In the case of chemical vapor deposition, the reactive nature of the gases involved makes it necessary to use post-deposition measurement techniques. After deposition, measurement of metal film thickness can be performed directly

with a stylus profilometer or SEM cross-sectional views of the films. Indirect measurement methods include electrical measurement of sheet resistivity and employment of gravimetric methods.

In the case of surface profiling, a fine diamond stylus is drawn over the substrate surface [44,45]. In the measurement process, the stylus encounters a step where the film has been masked during deposition or etched after deposition. The height of the step is then detected by the variation in signal based on differential capacitance or inductance techniques. Films less than 1000 Å can be measured with this technique with an accuracy better than 100 Å.

Cross-sectional scanning electron microscopy (SEM) pictures are commonly used to analyze deposited film thickness as well as morphology. The Si wafers are scribed on the back side and fractured. The SEM image is taken along the fractured surface until a good view of deposited film-substrate interface is found. Actual film thickness is determined from the magnification level. A reasonable difference in the brightness level, thereby the work functions, of substrate and film is essential in this technique.

The sheet resistance measurement technique is explained in detail in section "Sheet Resistance". This method assumes that deposited metal has the same resistivity as the bulk metal that also includes the same porosity, crystal structure,

and composition [46]. Films thinner than about 1000 Å are normally measured with this technique.

The gravimetric method is simply to weigh the substrate before and after film deposition by using a microbalance [44]. If the film is assumed to have a bulk density of ρ_b , the thickness is found by

$$\delta = \frac{\Delta m}{\rho_b A} \quad (17)$$

where, Δm is the increase in mass and A is the area. Note that Δm can also be obtained by etching the deposited samples. This method is explained in the experimental section.

Chemical Vapor Deposition

Chemical vapor deposition (CVD) is the deposition of non-volatile solid film on a substrate by chemical reaction of gaseous reactants [47]. The reactants enter the reaction chamber in gaseous form and react upon reaching the hot substrate surface to form the film. Many refractory materials such as metals, metalloids, oxides, carbides, borides, nitrides, silicides, and sulfides can be deposited by chemical reaction of gaseous reactants. One can use the CVD process to deposit essentially amorphous or microcrystalline materials as well as two- or three-dimensionally large single-crystalline materials.

VLSI fabrication technology utilizes CVD in a variety of areas such as the epitaxial growth of single-crystal silicon films, and the deposition of amorphous and polycrystalline thin films. CVD of refractory metals and their silicides is of special interest for the metallization process.

CVD metals formed by hydrogen reduction of metal halides are of importance for two reasons [48]:

- (1) The randomly oriented fine-grained material is useful for many structural shapes and the convenience of vapor forming makes it economical.
- (2) Preferentially oriented metal (especially W) has a uniform electron or ion emission property.

In summary, CVD processes offer a number of advantages over other deposition processes [47]. These advantages are:

- (a) It is possible to deposit high purity films.
- (b) Films with a wider range of chemical compositions can be attained.
- (c) CVD delivers the required film properties for some materials where other methods are inadequate.
- (d) For many films, the CVD process is economical and easier to control.

Applications of CVD films in VLSI technology include a variety of basic insulators, semiconducting layers, conducting layers, and superconducting films. Among the most commonly used films are silicon dioxide (SiO_2), silicon nitride (Si_3N_4), and polysilicon (Si). CVD films are expected to meet requirements for both the efficiency of the manufacturing steps and the final device performance.

Basic Steps in CVD

A CVD process basically is a type of surface catalysis process since the deposition process is thermodynamically favorable and takes place on the substrate surface. Most of the time the surface serves as a catalyst for the reactions leading to deposition and crystal growth. The same sequence of events in a heterogeneous reaction can therefore be applied to crystal growth by CVD [47,49]. These events are:

- 1) Introduction of reactant gases and diluent inert gases into the reaction chamber.
- 2) Transport of reactants to the substrate surface.
- 3) Adsorption of reactants on the surface.
- 4) Surface processes such as surface diffusion of adatoms, chemical reaction, and site incorporation.
- 5) Desorption of gaseous by-products.
- 6) Transport of gaseous by-products to the main gas stream.
- 7) Removal of by-products from the reaction chamber.

Experimental Parameters in CVD

Any one of the several steps taking place in a CVD process can be the rate-determining step. A number of experimental parameters play an important role in determining or altering the rate-determining step. The experimental parameters, which are discussed individually below are: deposition temperature, gas flow rate, crystallographic orientation, substrate position, reactant partial pressure, and surface area.

Deposition Temperature: Surface-reaction rate expressions can be written as a product of temperature- and pressure-dependent terms as

$$\text{Rate} = f_1(\text{Temperature}) f_2(\text{Composition}) \quad (18)$$

The temperature-dependent term is usually expressed by the Arrhenius equation

$$R = R_0 e^{(-E_a/kT)} \quad (19)$$

where, R is the rate constant at temperature T , R_0 is the frequency factor, k is the Boltzmann constant, and E_a is the activation energy for the process. Activation energy signifies the presence of an energy barrier which must be overcome in order for the process to occur. Adsorption, desorption, surface reaction, and surface diffusion can be described in this way as they involve activated reactions with the surface.

Activation energies for most surface processes are usually greater than 10 kcal/mole (0.43 eV/atom) and lie in the range of 25-100 kcal/mole (1.08-4.34 eV/atom) [49]. Exceptions to this generalization are reported in the literature [50].

Conversely, mass transport phenomena such as diffusion are almost insensitive to temperature. The temperature dependence of diffusion coefficients for molecular species is given as T^m , where m is between 1.5 and 2 [49]. Such a dependence yields small values (3-8 kcal/mole or 0.13-0.35 eV/atom) when plotted as an Arrhenius expression to find activation energies. Therefore, a preliminary distinction between the surface phenomena and the gas phase mass

transport phenomena can be made by observing the temperature dependence of the process.

An Arrhenius plot is a semilogarithmic plot of the rate constant (or rate for a fixed flow rate - or concentration - of reactants) versus reciprocal of the temperature. At lower temperatures, a classical Arrhenius plot exhibits a straight line which has a slope proportional to the activation energy of the surface reaction as shown in Figure 13. In this region, there is always enough supply of reactants to the surface and this supply is faster than the consumption of the reactants during the reaction. Then the overall rate is controlled by the surface kinetics. As the temperature is increased, the increase in surface reaction rate reaches such a level that the rate of mass transfer of reactants from the bulk to the surface becomes insufficient. A further increase in the temperature does not significantly increase the reaction rate because the rate is limited by the rate at which reactants are supplied to the surface. Then it is said that mass transfer is the rate-controlling mechanism. However, one should be very careful in stating a mass-transfer limited regime without corroborating evidence, for the Arrhenius plot gives the same behavior when there is not enough supply of reactants to the reactor, or when the reactant desorption rate becomes larger than the adsorption rate [51].

Thermodynamic aspects of the reaction system should also be considered when examining an Arrhenius plot. It is known

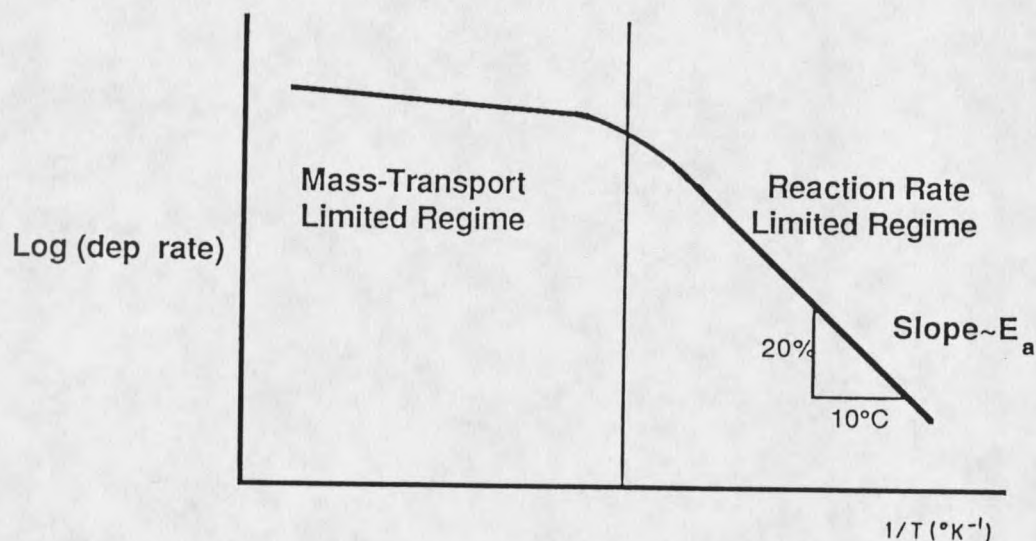


Figure 13. Temperature dependence of growth rate for CVD films [47].

that equilibrium processes exhibit rate-temperature variations which can be predicted from thermodynamic data [49].

Figure 14 illustrates the variation of rate with reciprocal temperature for different values of the heat of reaction; zero in curve B and negative in curve A (exothermic). At high temperatures, curve B approaches a slope where the rate is proportional to $T^{1.5}$, indicating a mass transport control. However, in curve A the rate decreases at temperatures higher than $\sim 750^\circ\text{C}$, indicating a thermodynamic limitation.

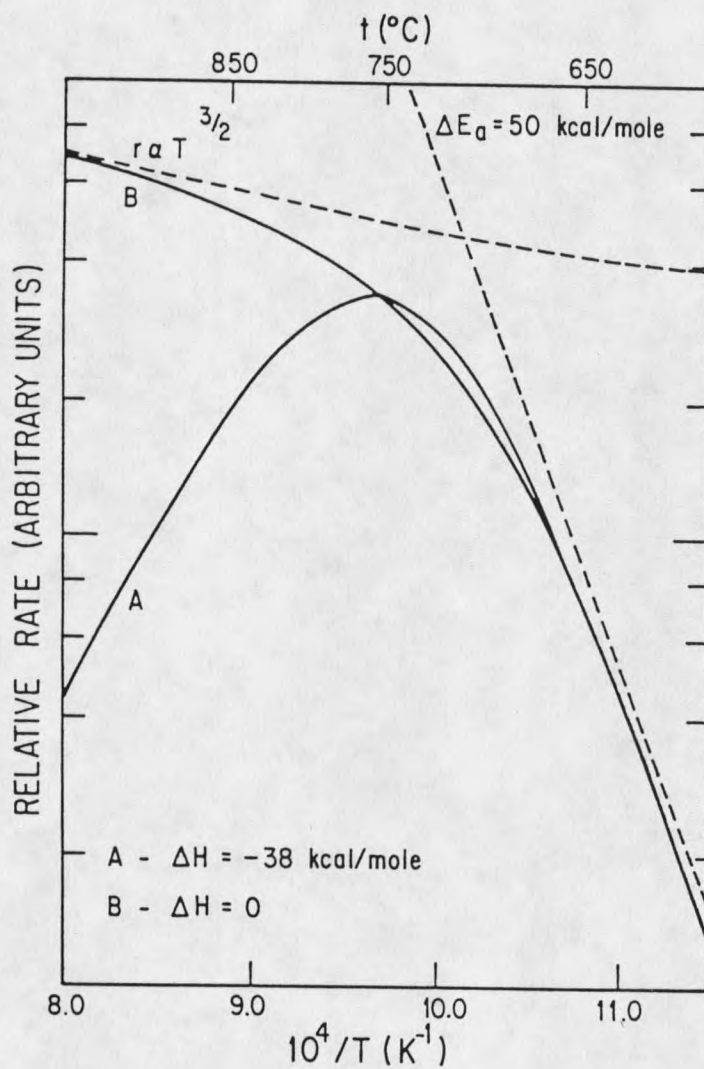


Figure 14. Reaction rate as a function of reciprocal temperature for zero and negative heat of reaction [49].

Figure 15 shows how the Arrhenius plot could change with changing positive values of the heat of reaction (endothermic). The increase of rate with temperature, in this case, is determined by the thermodynamics of the process rather than by the kinetics. Therefore, a high apparent activation energy does not necessarily indicate control by reaction kinetics.

Concentration dependence of the heat of sorption may also contribute to the activation energy. The procedure to find the true activation energies for this case is given in the literature [52]. Nevertheless, high activation energies strongly support kinetic control for exothermic processes [49].

Gas Flow Rate: When a linear growth rate for a CVD process is plotted as a function of reactant gas flow rate, the generalized form of the relationship is shown in Figure 16 [53]. At very small flow rates (Region I), the incoming gas stream has sufficient residence time to equilibrate with the substrate surface. Increasing the total flow rate increases the rate of reactant input, and thus more material per unit time equilibrates with the substrate surface. The rate increases linearly with total flow rate in this region [54].

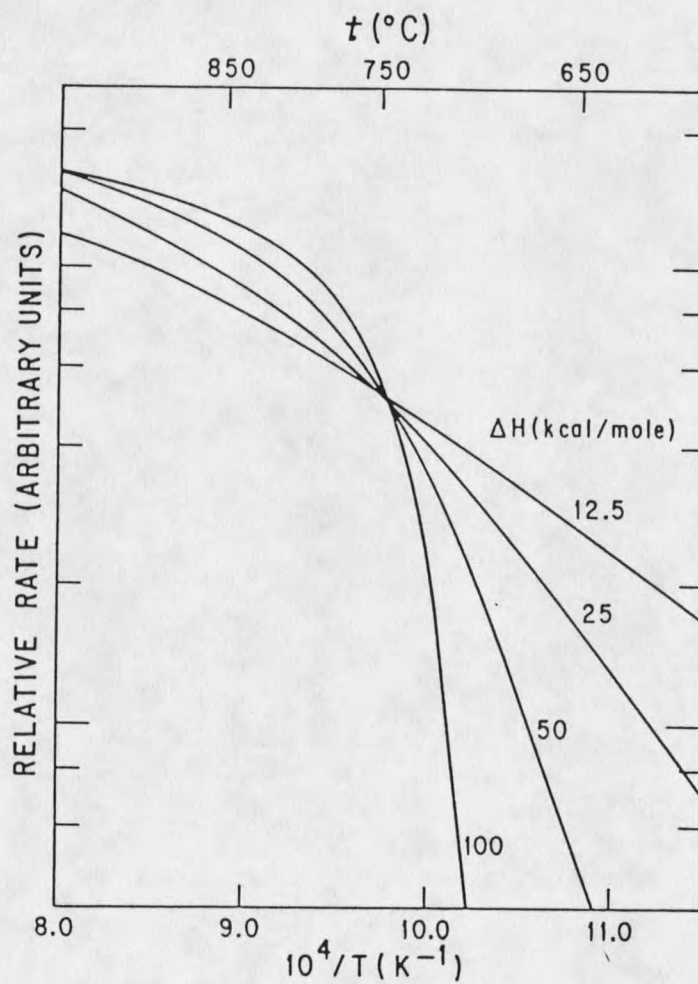


Figure 15. Reaction rate as a function of the reciprocal temperature for positive heat of reaction, illustrating erroneous apparent activation energies [49].

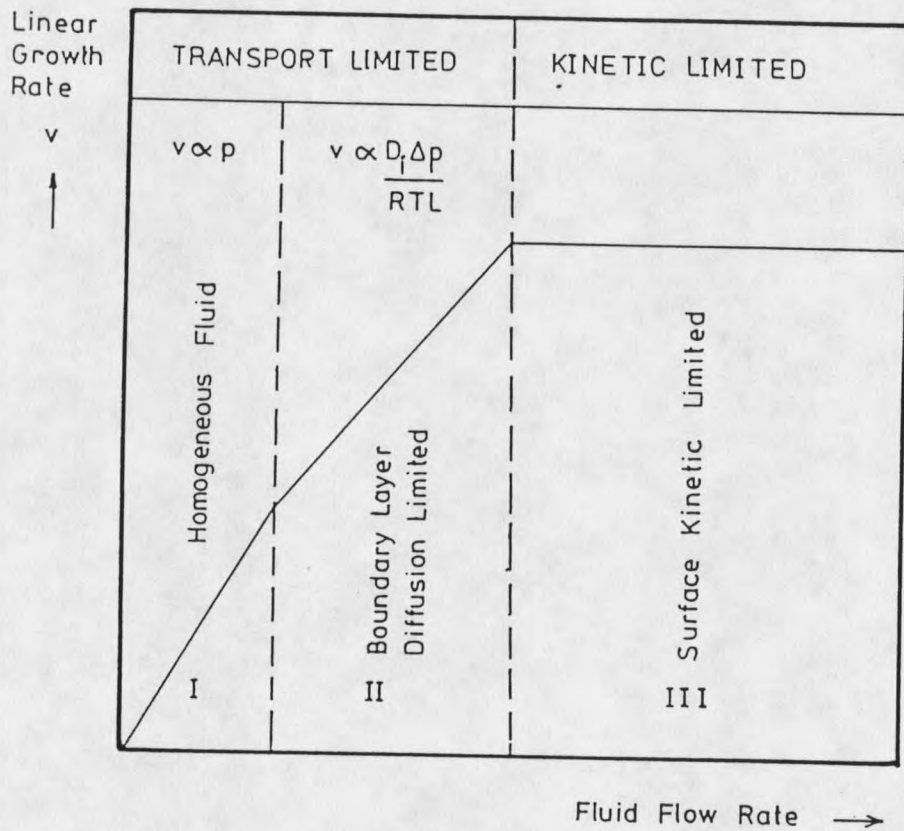


Figure 16. Idealized growth-rate versus fluid flow-rate plot showing the different growth regimes [53].

When the flow rate is increased above a certain point, the entire gas stream no longer has sufficient residence time for complete equilibration (Region II). At this point a portion of the incoming reactants pass by unreacted. This gives higher bulk stream partial pressures than the surface partial pressure. Then the rate-limiting process is diffusion from the main gas stream to the substrate surface. It is known that the boundary layer thickness, where the diffusion process takes place, is inversely proportional to the square root of the gas velocity [55,56]. Then, in this regime, the surface reaction shows a square root dependence on the gas flow rate.

At high flow rates, the reaction rate reaches a plateau (Region III) and becomes independent of flow rate [56]. Here the reaction rates are so slow relative to the gas flow and mass transfer rates that the partial pressure at the surface becomes essentially the input partial pressure. Then the process is said to be "kinetically controlled". The reactant flow rate for kinetic studies should be in this plateau regime so that the true temperature and partial pressure dependence of the reaction can be observed.

Crystallographic Orientation: Adsorption, desorption, and surface reaction are surface phenomena which involve surfaces chemically or take place on them. Different crystal orientations of a surface display different atomic arrangements and densities. As a result, the nature of the

surface has an effect on the rates of surface processes. For example, for GaAs deposition with surface kinetics controlling, the {111}A orientation has grown 16 times faster than {111}B orientation [57]. These two orientations have the same atomic density and geometry. The only difference is that one is terminated in a layer of Ga atoms and the other in a layer of As atoms. Effects resulting from the chemical differences of these two are called polarity effects. The relative rates of polar orientations can be altered considerably by changing the vapor concentrations or reactant ratios [58,59]. Surface diffusion rates are also reported to depend on crystallographic orientation [60].

Substrate Position: A change in substrate position may alter the flow patterns in the reactor which in turn influence the boundary layer thickness development and reactant distribution across the substrate surface. In principle, kinetically limited processes are independent of flow pattern changes. Mass transport (diffusion) controlled processes, however, are susceptible to changes in the flow dynamics [49]. Thickness uniformity of the deposited film can be significantly changed by altering the substrate position. Therefore, rate variations with substrate position offer support for diffusion control.

Reactant Partial Pressure: For simple processes, both diffusion and kinetic steps are first order in the reactant partial pressure. Therefore, first order dependence cannot be used to evaluate the rate limitations [49]. The dependence of reaction rate on reactant partial pressure can be used to characterize the reaction mechanism when the process is kinetically controlled. A basic error found in the CVD literature, including the $\text{SiH}_4\text{-WF}_6$ system, is that partial pressure dependence of some reaction systems have been reported while the reaction systems are shown to be mass-transport limited [49].

Surface Area: A surface reaction rate constant is a function of the actual surface area [49]. Initial substrate surface roughness or porosity developed in the depositing film will increase the actual surface area for reaction and give higher rates.

Chemical Vapor Deposition Reactors

Chemical vapor deposition reactor design depends on operating conditions of the deposition process and can be categorized according to two basic criteria [12,47]:

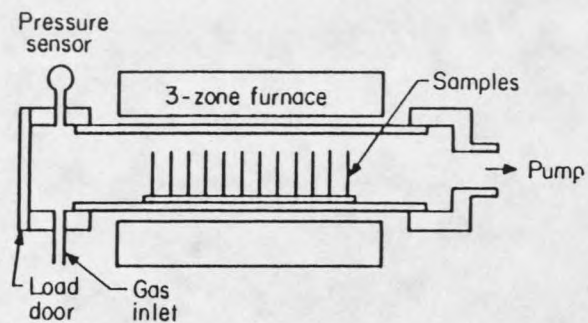
(1) Depending on the method used to heat the wafers, it can be either a hot-wall or a cold-wall reactor. (2) Operation pressure regime is also used in grouping terminology such as atmospheric pressure or reduced pressure reactors (Figure 17).

Heating methods for wafers are resistance heating, rf induction heating, energy from a glow discharge (plasma), and photons.

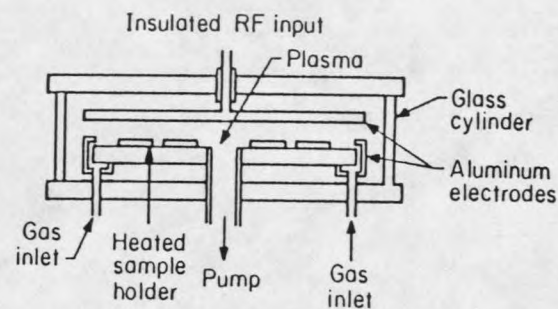
Hot-wall Reactors: A hot-wall reactor is essentially a quartz tube heated by resistance-heating coils surrounding the reaction tube. In this way, not only the wafer but also the reactor walls are hot, and that results in deposition on the interior walls. This, in turn, may cause reactant depletion on the wafers. Wafers stand vertically, perpendicular to the gas flow, in a quartz holder. Hot-wall reactors allow good throughput, large wafer diameters and good film uniformity. The disadvantages are the requirement of frequent cleaning, relatively low deposition rates due to reduced pressures and frequent use of toxic, corrosive or flammable gases [61].

Cold-wall Reactors: When the heating is done via rf induction or infrared lamps mounted in the reactor, it stays restricted to the wafers and susceptor [47]. In this case, the reactor walls essentially stay cold and the reactor is called a cold-wall reactor.

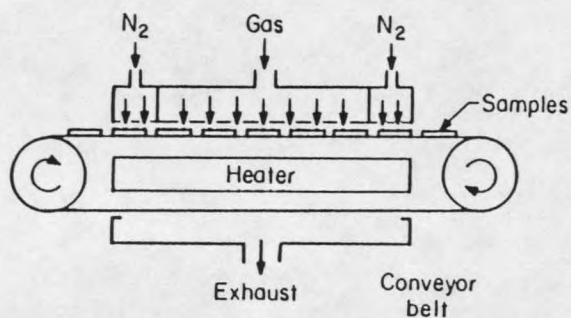
Atmospheric Pressure Reactors: Atmospheric pressure chemical vapor deposition (APCVD) reactors are easier to design and they provide relatively high deposition rates [62]. Operation is in the mass-transport limited regime. This limits



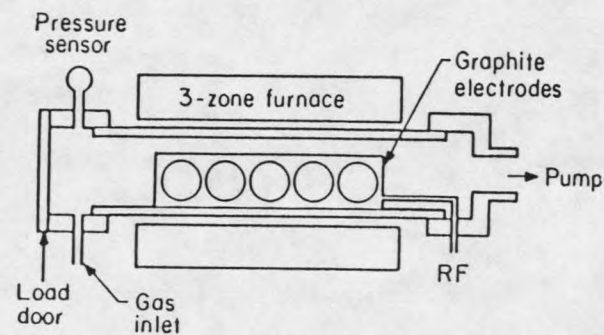
(a)



(c)



(b)



(d)

Figure 17. Schematic diagrams of CVD reactors. (a) Hot-wall, reduced-pressure reactor. (b) Continuous, atmospheric-pressure reactor. (c) Parallel-plate. (d) Hot-wall. [12]

the flexibility in reactor geometry as it is necessary to supply reactants on the substrates uniformly throughout the reactor. APCVD reactors are used for low-temperature oxide (LTO) deposition and epitaxy [47].

Horizontal tube APCVD reactors are hot wall reactors and are used very little in VLSI processing. Their disadvantages are low throughput, poor thickness uniformity, and particulate contamination.

Continuous processing APCVD reactors can provide better thickness uniformity, low contamination, and high throughputs. In the process, the wafers are moved at a constant speed through the heated section by means of a plate or a conveyor belt. Reactant gases flowing through the reaction zone are isolated from outside air by curtains of flowing gas. These reactors require very fast gas flows and need frequent cleaning.

Low-pressure CVD Reactors: Low-pressure chemical vapor deposition (LPCVD) reactors operate at medium vacuum (30-250 Pa or 0.25-2.0 Torr). Reduced pressure increases the gas phase diffusivity and reduces the mass-transfer restrictions for the deposition reaction. Therefore, LPCVD reactors operate more in the reaction-rate limited regime. Elimination of mass-transfer limitations provides high wafer capacity, better thickness uniformity and less gas phase reactions (i.e. less particulate contamination) [63]. The disadvantages are the low deposition

rates and the relatively high operation temperatures. There are two main design configurations of LPCVD reactors, horizontal tube and vertical flow isothermal.

Horizontal tube LPCVD reactors are hot-wall reactors and are widely used for depositing poly-Si, silicon nitride, and undoped and doped SiO_2 films [47]. They are superior in terms of economy, throughput, uniformity, and ability to accommodate large diameter wafers. However, they provide low deposition rates and still are susceptible to particulate contamination [61]. As mentioned earlier, LPCVD reactors operate in the reaction-rate limited regime, therefore equal mass transport to all parts of every wafer is not critical. Wafers are therefore stacked vertically at very close spacing. Compared to APCVD, the gain by a larger number of wafers being processed far outweighs the loss by lower deposition rates; the net result is a higher throughput for the LPCVD reactor. Reactants are fed from one end of the tube and are pumped out from the other end. Depletion effects are still observed towards the end of the tube as reactant concentration decreases. This can be compensated either by linearly increasing temperature in the direction of flow or by introducing the reactants at several points along the tube length. The latter arrangement is known as distributed feed.

A vertical-flow isothermal LPCVD reactor is the improved form of the distributed gas feed technique on a cold-wall reactor [64]. Wafers are stacked in perforated quartz cages

and the gases are introduced through the perforations. In this way, identical quantities of fresh reactants are supplied to each wafer. This design allows highly uniform depositions with low particulate contamination.

Plasma-enhanced CVD Reactors: The method of energy input for the deposition reaction is also used in the grouping terminology for CVD reactors. Plasma enhanced CVD (PECVD) reactors utilize plasma (glow discharge) created by an rf induction onto a low pressure gas [47]. Since the reactant gases are more reactive in the plasma state than the neutral state, PECVD is carried out at substrate temperatures lower than those of APCVD and LPCVD process. The radicals formed in the plasma discharge have high sticking coefficients and upon adsorption they can migrate easily on the surface to yield conformal structures. Films with low pinhole density and with good adhesion to the substrate can be deposited with this method. PECVD reactors are widely used for the deposition of silicon nitride and SiO_2 over metals. PECVD films are not stoichiometric because of the complexity of the reaction and are contaminated with by-products and incidental species. These contaminants cause problems in later stages of manufacturing MOS circuits. When compared to an LPCVD process, the PECVD process is dependent on additional parameters such as rf power density, frequency, and duty cycle.

There are three basic types of PECVD reactors: (1) the parallel plate type, (2) the horizontal tube type, and (3) the single wafer type.

Photon-induced CVD Reactors: Photon-induced chemical vapor deposition (PHCVD) uses high-energy, high-intensity photons either to excite the reactant gases or to heat the substrate surface [47]. Good step-coverages at low temperatures are possible with this method but contamination of films is the main disadvantage. A UV lamp or laser is used as energy source [65]. Extremely low deposition rates make PHCVD reactors infeasible for the microelectronic industry.

Chemical Vapor Deposition of Tungsten

It was in the early 70's that polysilicon technology started to be widely employed in the fabrication of metal-oxide semiconductor (MOS) VLSI circuits. The advantages were compatibility with silicon wafer processing, the capability of self-aligning features, stable and controllable gate electrode characteristics, applicability of simple deposition techniques such as CVD, and narrow linewidths readily patterned with selective dry etching processes [66].

Figure 18 shows address access times for polysilicon and refractory metal gates as a function of gate length [67]. For a polysilicon gate, decreasing gate lengths down to 2 μm gives decreasing gate address access time, which results in shorter signal processing time. However, below 2 μm , access time increases with decreasing gate lengths. Here at very small dimensions, the high resistivity of polysilicon (20 ohm/square sheet resistance) projects the impact of RC delay time on circuit performance. RC delays are defined as delays caused by resistance and capacitance of interconnect lines. On the other hand, a refractory metal silicide gate (1 ohm/square sheet resistance) gives smaller access times with decreasing gate lengths even below 2 μm . This limitation of polysilicon forced researchers to explore the employment of refractory metals such as tungsten (W) and molybdenum (Mo) as gate electrodes and interconnections in metal-oxide semiconductor field-effect

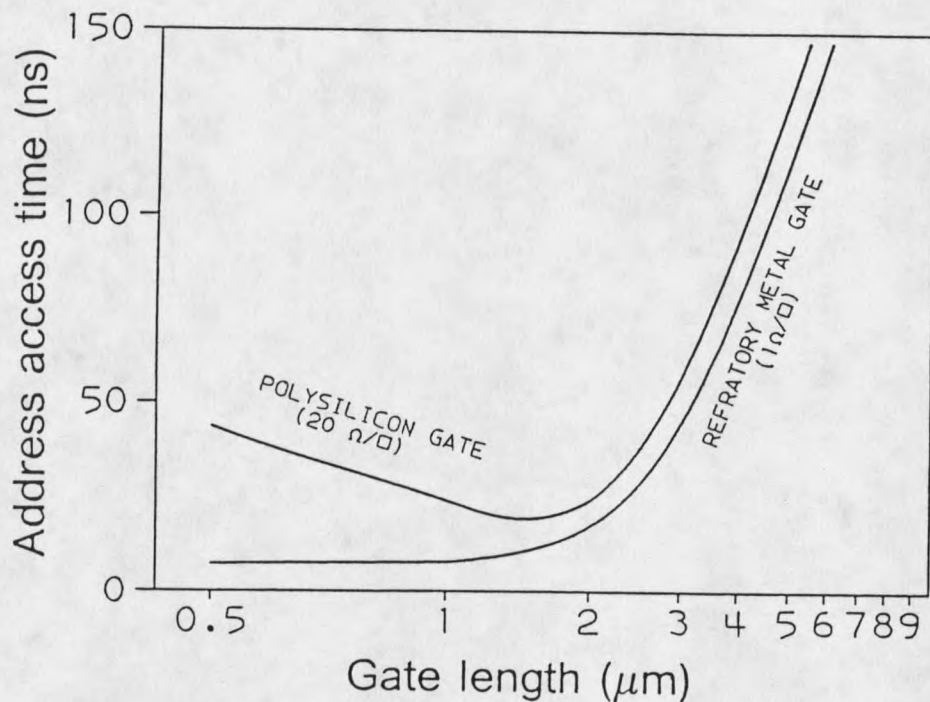


Figure 18. Address access time as a function of gate length. For geometries below $2\mu\text{m}$, access time for 4K static NMOS RAMs are improved by using refractory metal gates [67].

transistor (MOSFET) technology. Starting from late 1960's the feasibility of refractory silicides as a replacement for polysilicon was explored [68-70]. In 1983, VLSI technology utilized polycides deposition by co-sputtering of molybdenum or titanium silicide [66]. (The term polycide is used for a multilayer structure, consisting of a low resistance material, such as refractory metal silicide, on top of a doped polysilicon layer.) However, the technical difficulties

associated with co-evaporation techniques directed manufacturers to switch to the LPCVD process. In 1986, the first volume production of 1 M DRAM used tungsten silicide deposition by LPCVD.

As ultra-large scale integration (ULSI) is becoming a reality, the dimensions are decreasing to sub-micron levels. Silicide films at these thickness levels cannot produce a low enough sheet resistance to meet the demands for device performance. Thus, a lower resistivity advantage of metals over metal silicides makes metallized polysilicon and metallized source/drain regions attractive [71]. Selective metal deposition has been a special interest for its self-aligning, self-patterning capability [72].

CVD tungsten was accepted as an excellent interconnect material and applications at production level have already started. Tungsten provides low resistance ($5.6 \mu\Omega\text{-cm}$ of bulk resistivity), low stress ($<5 \times 10^9 \text{ dyn/cm}^2$), excellent conformal step coverage and a thermal expansion coefficient which is close to that of silicon. Another important feature for tungsten is its high resistance to electromigration, while in the current technology aluminum severely suffers from it. CVD tungsten films can also form low resistance contacts to silicon. Figure 19 gives the potential applications of CVD tungsten. The use of tungsten as interconnect metal improves the wirability in the circuit and hence reduces wiring delays. The incorporation of vertical vias into the structure improves

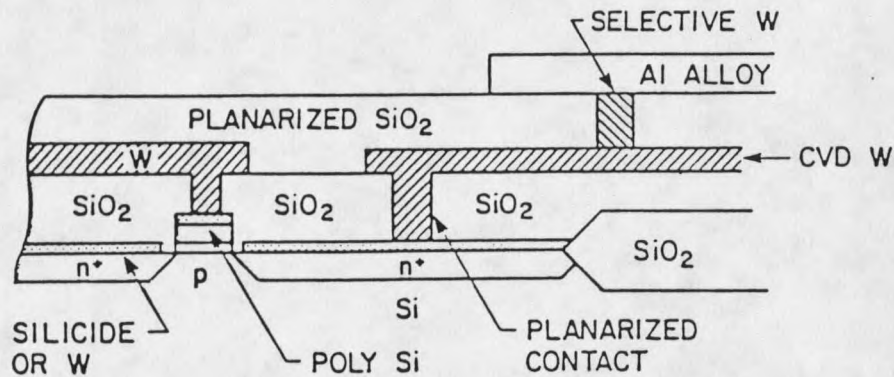


Figure 19. Future applications of refractory metals and/or metal silicides. Future applications include metallized source/drain regions and polysilicon, selective W in vertical vias, and CVD W for first level metal [66].

the circuit density and performance by decreasing wiring delay.

Reactions for CVD of Tungsten

Tungsten hexafluoride (WF_6) is the common W source gas for the chemical vapor deposition of tungsten. It can be reduced with silicon (Si), hydrogen (H_2), or silane (SiH_4). Tungsten hexachloride (WCl_6) is another source of W, and is used in a hydrogen reduction reaction. The free energy

Table 1. Free Energy Changes at 600 K [7].

Reactions	ΔG , kcal/mol
1) $WF_6 + 1.5Si \rightarrow W + 1.5SiF_4$	-179.4
2) $WF_6 + 3H_2 \rightarrow W + 6HF$	-27.9
3) $WF_6 + 1.5SiH_4 \rightarrow W + 1.5SiF_4 + 3H_2$	-208.7
4) $WF_6 + 2.1SiH_4 \rightarrow 0.2W_5Si_3 + 1.5SiF_4 + 4.2H_2$	-227.6
5) $WF_6 + 3.5SiH_4 \rightarrow WSi_2 + 1.5SiF_4 + 7H_2$	-268.9

changes, ΔG , for WF_6 reactions at 600 K are given in Table 1 [7].

The Si reduction reaction yields tungsten films by consuming the exposed Si substrate. The reaction stops after a certain W film thickness is reached; this characteristic is called self-limiting. Once the limiting thickness is reached, the W film forms a diffusion barrier between the Si and WF_6 , and prevents further reaction. Films thicker than the limiting thickness can be deposited with the H_2 reduction reaction. Selective deposition of tungsten is also possible with both Si and H_2 reduction provided that certain temperature, pressure and flow conditions are met. When the H_2 reduction reaction is carried out, it is the Si reduction reaction that takes place first. The reason is that the negative free energy change for the WF_6 -Si reaction (-179.4 kcal/mol) is much larger than that for the WF_6 - H_2 reaction

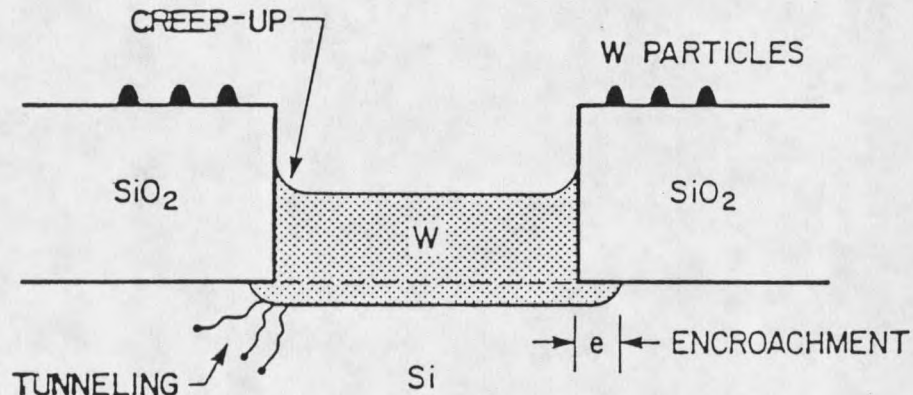
(-27.9 kcal/mol). This implies that the Si reaction can only be suppressed after the Si surface is coated with W by the Si-WF₆ reaction. Thus, the W/Si interface morphology is dictated by the Si reduction reaction. Since the Si reduction results in Si consumption, the junction may be damaged or broken. Figure 20 illustrates the common problems associated with selective W deposition by LPCVD. The problems such as encroachment, tunneling, creep-up, and loss of selectivity may either degrade the device quality or cause a complete failure.

The SiH₄ reduction reaction ($\Delta G = -208.7$ kcal/mole) is more favorable than the Si and H₂ reduction reactions. This reaction can suppress the Si reduction reaction and Si consumption. Higher deposition rates at relatively lower temperatures and smoother resulting W/Si interfaces make this reaction very attractive, especially for blanket W deposition. The problems such as tunneling and encroachment can be avoided with this reaction. Table 1 suggests that the SiH₄/WF₆ ratio should be kept below 1.5 to prevent any tungsten silicide (WSi_x) formation.

Background about each reduction reaction is given below.

Si Reduction of WF₆

There have been limited studies to evaluate the reaction mechanism of WF₆ by directly reacting with the silicon substrate. This reaction can be used to produce thin films of selectively deposited W. Most researchers observed a limiting



SELECTIVE LPCVD TUNGSTEN

Figure 20. Schematic illustration of several problems associated with selective W deposition by LPCVD [66].

deposit thickness, after which no further deposition took place. Morosanu and Soltuz [73] reported a linear dependence between tungsten growth rate and time; however, this behavior was not confirmed by others, as discussed later. Tungsten films were less than 10,000 Å thick and were deposited in an atmospheric CVD system.

Melliar-Smith, et al. [5] carried out the Si reduction of WF_6 in an inert atmosphere and found a limiting tungsten thickness of 300-400 Å in a temperature range of 420-880°C. In high flow atmospheric deposition conditions, Sauermann and

Wahl [74] have recorded limiting tungsten film thicknesses changing with deposition temperature. Limiting tungsten film thicknesses between 150 and 400 Å were also observed by Saraswat, et al. [75] and Moriya, et al. [76].

Busta and Wu [77] carried out experiments on single-crystal silicon wafers with native oxide thickness ranging from 3 to 60 Å. They were able to deposit 400-500 Å thick films on 12-15 Å thick native oxide layers. Above 40 Å thick native oxide, the W film thickness was practically zero. Tsao and Busta [78] observed a strong dependence of W film thickness on the precleaning procedure of silicon surfaces. They also recorded a decrease in thickness from 700 Å (maximum thickness) to 200 Å when the temperature was raised from 420°C to 500°C for polysilicon (440°C for single-crystal silicon). This decrease was explained as the etching of films by WF_6 which is catalyzed by the presence of phosphorus, present from doping. They proposed that the temperature dependence of the sticking coefficient of a reactive intermediate controls the reaction.

Broadbent and Ramiller [6] have spanned a pressure range of 0.1-5 torr and a temperature range of 300-425°C in their studies. They reported that a limiting tungsten thickness forms in as little as 0.1 min deposition time. At the beginning, the WF_6 -Si reaction occurs at a rate of at least 1000 Å/min until a limiting thickness of 100-150 Å is reached. Recorded tungsten film thicknesses were scattered within the

limiting values and under no conditions did they observe a linear dependence of film thickness on reaction time. The thickness was shown to be independent of the temperatures studied. Tungsten films were comprised of monocrystalline W grains. Nonuniformities in the thickness were attributed to the presence of a varying initial oxide layer on the Si substrate.

McConica and Krishnamani [79] have examined the silicon reduction of tungsten hexafluoride for a temperature range of 288-403°C and tungsten hexafluoride partial pressure range of 0.5-5 torr. The limiting thickness was between 100-400 Å and independent of time, temperature and WF_6 partial pressure. Electron spectroscopy for chemical analysis (ESCA) results showed oxygen in the films, which was believed to be the reason for the high resistivity. In every case the thickness was self-limiting. Similar to the findings of Broadbent and Ramiller [6], no linear dependence of film thickness on deposition time was observed.

Yu, et al. [80] have found that thermal annealing can cause the silicon atoms to diffuse through the tungsten film and segregate on the tungsten surface. Liftshitz [81] proposed that the formation of non-volatile lower fluorides of tungsten (where the most likely is tungsten tetrafluoride, WF_4) is responsible for the self-limiting effect. This hypothesis was supported by secondary ion mass spectroscopy (SIMS) results.

Raupp and Hindman [82] performed temperature programmed reaction (TPR) studies of WF_6 decomposition on Si(100) and W/Si(100) surfaces in ultra high vacuum (UHV) conditions. They observed that deposited tungsten rapidly chemisorbed WF_6 , and above 300K tungsten and silicon interdiffused. Clean bulk W readily dissociates and strongly adsorbs hydrogen; conversely, chemical vapor deposited tungsten (CVD-W) did not readily chemisorb hydrogen. Tungsten hexafluoride adsorbed less strongly on a native silicon dioxide surface, but was capable of partially reducing this thin oxide layer.

Green, et al. [83] examined the morphology of Si-reduced W films deposited between 210 and 700°C. The grains were spongy in structure, and the space occupied by trapped gases and pores was as high as 59%. Therefore, the film density was far less than tungsten bulk density.

Auger depth analysis showed that most of the oxygen in the W films is present at the Si/W [84]. Joshi, et al. [85] found 22-25% oxygen in the films deposited below 600°C, causing high film resistivities (130-140 $\mu\Omega\text{-cm}$). The oxygen level drops to 12-13% at higher temperatures resulting in lower resistivities (60-70 $\mu\Omega\text{-cm}$). A native oxide layer on the silicon surface was reported to be incorporated into the W films [78].

H₂ Reduction of WF₆

Tungsten can be selectively deposited on silicon, metal and silicide surfaces by the WF₆-H₂ reaction. SiO₂ and SiN₃ surfaces do not provide good nucleation sites for the deposition reaction. This property makes CVD tungsten by this reaction very attractive in integrated circuit manufacturing, because tungsten is deposited only on the desired surfaces. Selective deposition obviates the necessity for an additional masking, thus reducing the number of process steps and cost.

There have been quite a number of studies on the reduction mechanism of WF₆ in the presence of hydrogen. Holman and Huegel [86] obtained data regarding the effects of temperature, pressure, and vapor composition on the CVD reaction rate. Shroff and Delval [87] carried out tungsten and molybdenum deposition by the H₂ reduction of WF₆ and MoF₆ on copper, stainless steel and molybdenum surfaces. The H₂/WF₆ ratio was varied from 1 to 60 for a temperature and partial pressure range of 450-1200°C and 5-760 torr, respectively. For a constant H₂/WF₆ ratio, the deposition rate increased with total pressure, reached a maximum around 100 torr, then decreased. This maximum was observed to shift towards higher pressures as H₂/WF₆ ratio increased.

Cheung [3] interpreted the reaction as rate-limited by the activated adsorption of hydrogen. Further, H₂ dissociation is controlled by the jumping of one of the H atoms to a neighboring site. He also noted that HF desorption could be

rate-limiting under certain conditions. Bryant [4] stated that dissociation of H_2 molecules adsorbed on the substrate is the rate-limiting mechanism when gas phase diffusion limitations are absent.

Broadbent and Ramiller [6] examined the tungsten deposition rate as a function of substrate temperatures of 250-500°C and total pressures of 0.2-2 torr. The Arrhenius plots shown in Figure 21 exhibit a constant slope, signifying a congruent pattern of a rate-limiting reaction mechanism for the examined temperature and pressure range. The calculated activation energy of $E_a = 0.71$ eV/atom (69,000 J/mole) is very close to that previously reported as 0.69 eV/atom (67,000 J/mole) [3,4,86,88]. This is also the activation energy for surface diffusion of H_2 on W [89,90]. The tungsten growth rate shows a square root dependence on the total pressure ($R \propto P^{1/2}$) for constant H_2/WF_6 ratios. By keeping WF_6 partial pressure constant, the same square root dependence of the rate on hydrogen partial pressure ($R \propto P_{H_2}$) was also observed. The growth rate, however, was not dependent on the WF_6 partial pressure. These dependencies suggested that surface-adsorbed H_2 dissociation is the rate-controlling mechanism.

Another kinetic study performed by McConica and Krishnamari [79] used the same H_2/WF_6 ratio of 15 as did Broadbent and Ramiller [6]. The temperature and pressure ranges were 287-405°C and 0.2-10 torr, respectively. The activation

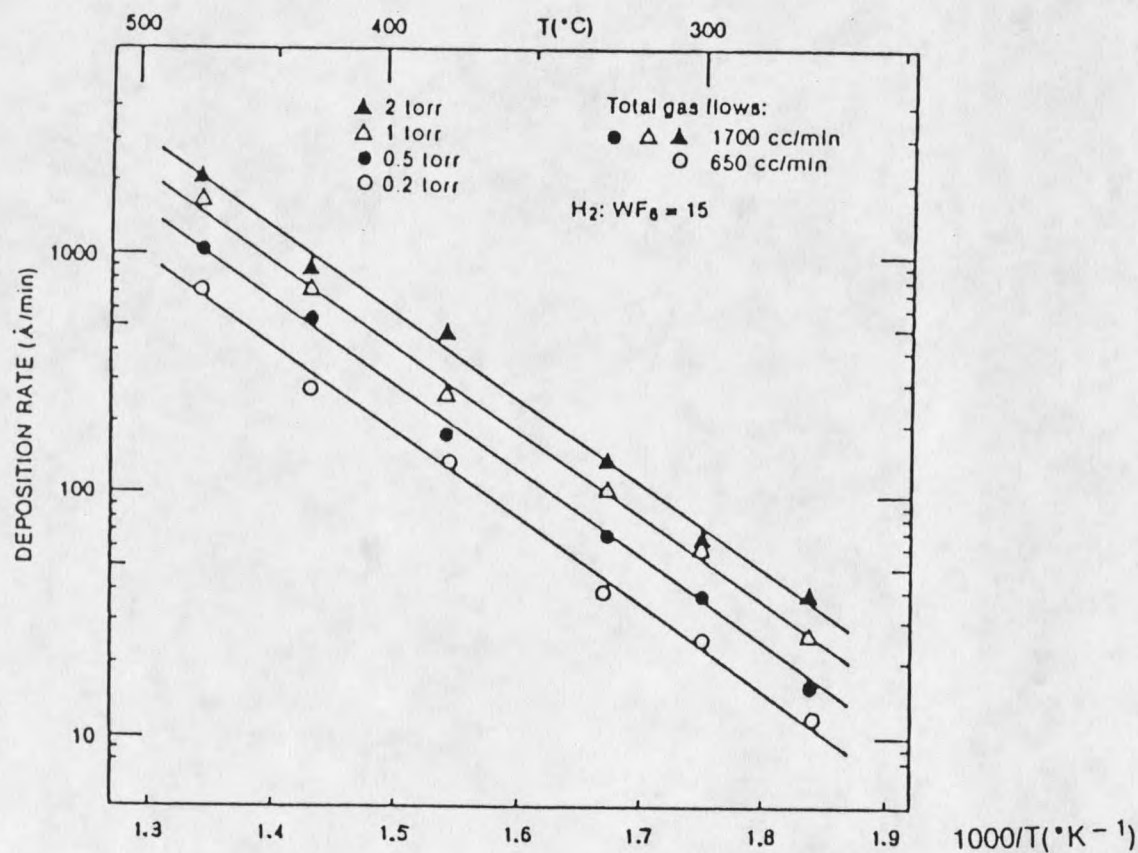


Figure 21. Arrhenius plot of deposition rate of CVD tungsten by H₂ reduction of WF₆ [6].

energy was reported as 0.76 eV/atom (73,000 J/moles), a higher value than previously reported. The growth rate was then expressed as

$$R = 6.8 \times 10^4 e^{(-8800/T)} (P_{WF_6})^0 (P_{H_2})^{0.5} \quad (16)$$

where, T is in K, P in Pa, and r in nm/s.

Selective deposition of W on Si surfaces constitutes another area of concern in the H₂-reduction reaction. Joshi, et al. [85] have found that the selectivity of tungsten produced by silicon reduction is almost 100% while that by H₂ reduction depends on the prior condition of the Si wafer. McConica and Krishnamani [79] observed that the selectivity loss to silicon surfaces occurs at temperatures higher than 300°C. The temperature dependence suggested that the tungsten nucleation on the oxide is an activated process. In a ultra high vacuum (UHV) analysis chamber, Creighton [91] performed Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) studies on the selectivity loss. He suggested that a tungsten subfluoride desorption-disproportionation mechanism is the origin of transport of tungsten from the tungsten surface to the silicon dioxide surface. Tungsten pentafluoride, WF₅, was the best candidate to initiate the selectivity loss because of its volatility.

Studies of the CVD tungsten film morphology and impurity content are essential for the film quality, and thereby the film resistivity. Shroff and Delval [87] have measured the

fluorine content of W films with photon activation analysis. The deposition of low fluorine content films was possible at high temperatures, high H_2/WF_6 ratios and low pressures. Initial tungsten layers always started with a fine grain structure on the base metal substrates and continued to grow as elongated crystals. It was also reported that increasing H_2/WF_6 ratios and higher pressures resulted in less adherent and inhomogeneous coatings. This was exacerbated at high temperatures due to nucleation in the vapor phase.

Paine, et al. [92] observed wormhole formation in the Si substrate. They also reported W/Si interfacial roughness, and lateral encroachment. McLaury, et al. [93] have found that fluorine was a major contaminant in the films. Transmission electron microscopy (TEM) studies revealed damage at the (100) Si/SiO₂ interface in the form of worm tracks. Stacy, et al. [94] performed TEM analyses on the W films and confirmed tungsten deposition filaments (also called wormholes or tunnels) in the silicon substrate. Joshi, et al. [85] stated that H_2 reduction produces purer films than Si reduction by gettering oxygen in the reaction chamber. Thus, the resistivities for H_2 reduced films (9-10 $\mu\Omega$ -cm) are far less than those of Si reduced films (130-140 $\mu\Omega$ -cm). They also noted that hydrogen reduction produces very rough films compared to silicon reduction.

The frequently observed preferential tungsten crystal orientation in the H_2 reduction reaction is W(100) [87]. High

H_2/WF_6 ratios have been reported to give W(111) orientation [95]. In a more detailed structural study, Kamins, et al. [96] examined orientation change with thickness for W films. They used a chromium nucleation layer to prevent the Si- WF_6 reaction from influencing the W film structure. Figure 22 shows (100) dominance increasing with film thickness. The increase in (100) texture correlated with the increase in grain size, implying that (100) oriented grains grow at the expense of those with other orientations. Near the standard operating temperature of 300°C, the structure was not a sensitive function of temperature.

SiH₄ Reduction of WF₆

The employment of silane chemistry in W deposition reduces the need for process fine-tuning. A single-step deposition process eliminates silicon consumption which appears in the form of encroachment and wormholes. Silane chemistry substitutes for the initial silicon reduction step, since silane is more reactive than silicon in reducing tungsten hexafluoride. Thus, the silicon interface is not affected by direct tungsten deposition reaction and remains smooth. In spite of the recent extensive studies on the tungsten film quality and deposition parameters, the kinetics of the SiH₄- WF_6 reaction system has not been understood well and literature on the subject is very scarce.

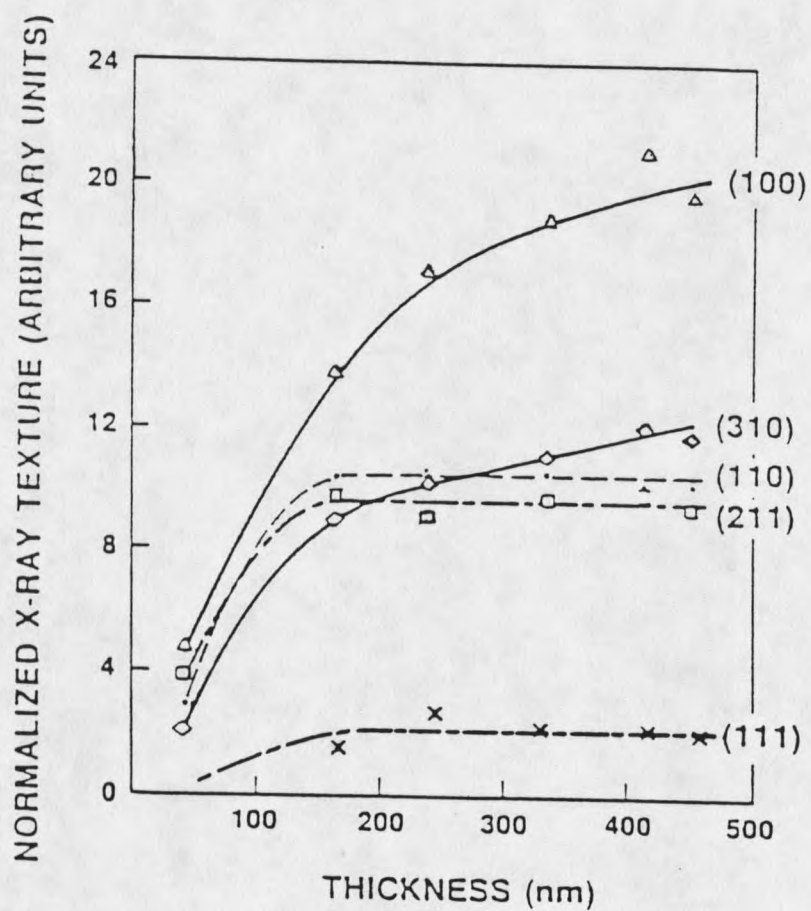


Figure 22. Normalized x-ray texture as a function of film thickness [96].

The first CVD literature on the SiH_4 - WF_6 system appears in 1973 by Lo, et al. [97]. Utilizing relatively higher pressures and temperatures ($P_{\text{total}} = 100$ torr, $T = 600$ - 800 °C) than is currently practiced in CVD-W process, they found that 1% Si in the films can break up the columnar structure of thick tungsten. The selective deposition of tungsten using WF_6 and SiH_4 was first examined in 1982 by Furuyama and Moriya [98]. They demonstrated that in a hot-wall system, much thicker W films can be grown using SiH_4 reduction instead of H_2 reduction. Several researchers have further studied SiH_4 reaction as an alternative to H_2 reduction of WF_6 [99-103].

Kusumoto, et al. [7] used TEM analysis to confirm that the tunnel formation can be eliminated when SiH_4 is used as the reducing agent in place of H_2 . The deposition was selective to Si when the SiH_4/WF_6 ratio was less than 1.5, and no tungsten silicide was formed until the ratio exceeded 2.1. The Arrhenius plots for the temperature range of 260-360 °C showed maxima, and the reason was speculated to be a change in the reaction mechanism (Figure 23). The deposition rate was not dependent on WF_6 partial pressure but on SiH_4 partial pressure. They noted that H_2 addition depresses the reaction since H_2 is a reaction product.

Ohba, et al. [8] studied the selective chemical vapor deposition of tungsten using silane and polysilane reduction of tungsten hexafluoride at a total pressure of 0.3 torr. At low temperatures, the reaction rate was up to three orders of

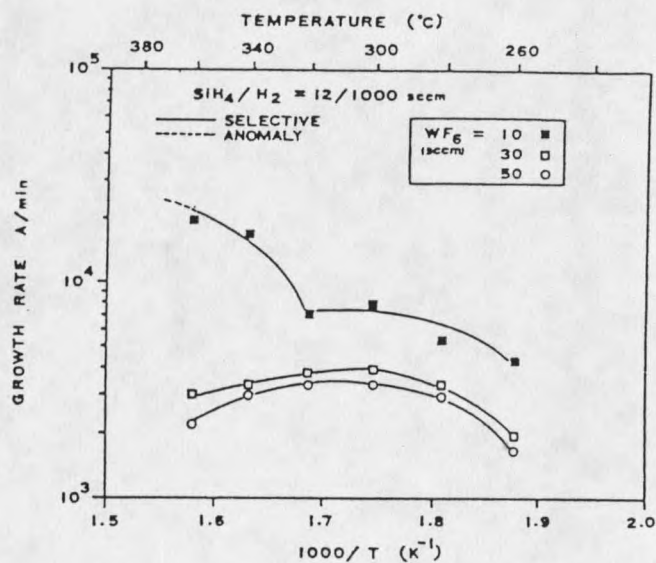


Figure 23. Arrhenius plots for $\text{SiH}_4\text{-WF}_6$ reaction system [7].

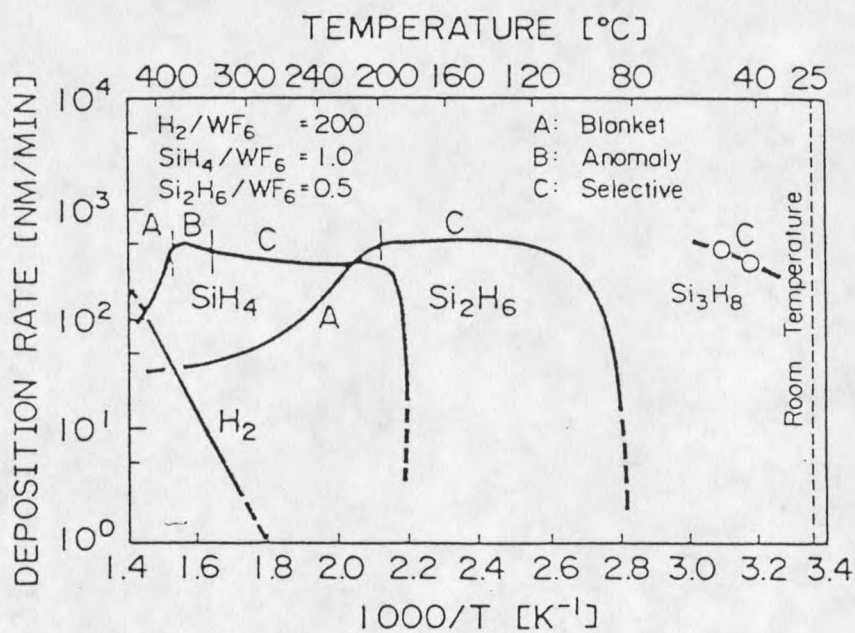


Figure 24. Arrhenius plot of H_2 and $\text{Si}_n\text{H}_{2n+2}$ ($n = 1-3$) reductions of WF_6 [8]: (A) blanket, (B) anomalous, and (C) selective deposition.

magnitude faster than that of H_2 reduction. There was no encroachment and leakage current of the resulting W deposit was low. They reported that the silane reduction reaction starts at around $180^\circ C$ and is mass transport limited within $180-280^\circ C$ range (Figure 24). The partial pressure dependence of the reaction was 1.3 with respect to silane ($R \propto P_{SiH_4}^{1.3}$) and 0.6 with respect to tungsten hexafluoride ($R \propto P_{WF_6}^{-0.6}$). The selectivity was lost at high SiH_4 partial pressures.

Schmitz, et al. [9] have performed experiments in a batch system to establish the kinetics of the SiH_4 reduction of WF_6 . They examined the temperature range between $250^\circ C$ and $550^\circ C$ under a total pressure of 0.075 torr. For SiH_4/WF_6 ratios less than 1.0, the rate expression was

$$R = \text{constant } (P_{WF_6})^0 (P_{SiH_4})^1 \quad (21)$$

However, the Arrhenius plot shown in Figure 25 is complicated, therefore they were not able to obtain an activation energy. Interpretation of the kinetic data led them to speculate that the homogenous dissociation of SiH_4 was the rate limiting step. In a subsequent study, Schmitz, et al. [104] reported that H_2 partial pressure as carrier gas has no influence on W growth rate or selectivity. This is in contrast with Kusumoto, et al. [7].

Rosler, et al. [10] have found that the selective W deposition rate was as high as $15,000 \text{ \AA/min}$ over the

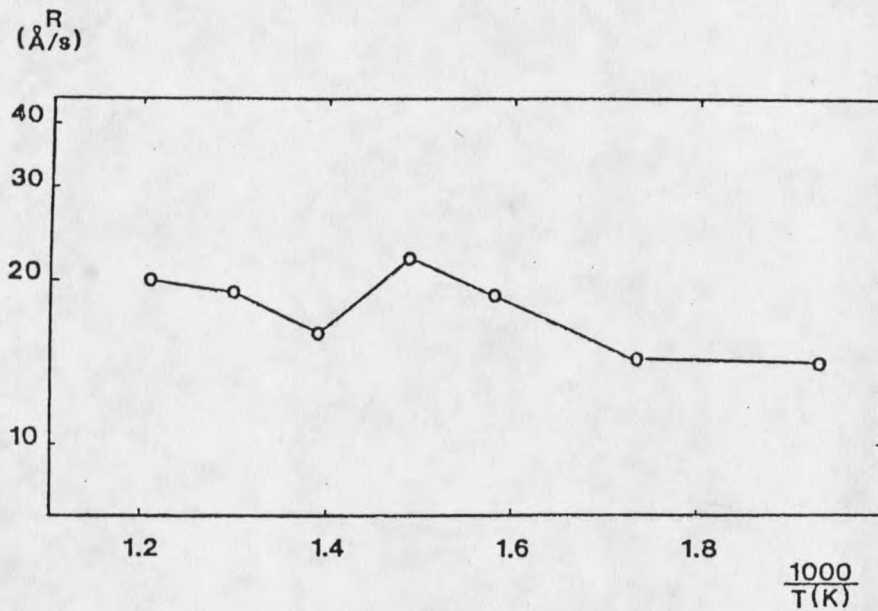


Figure 25. Arrhenius plot for $\text{SiH}_4/\text{WF}_6 < 0.9$ [9]. $P_{\text{tot}} = 75$ mtorr.

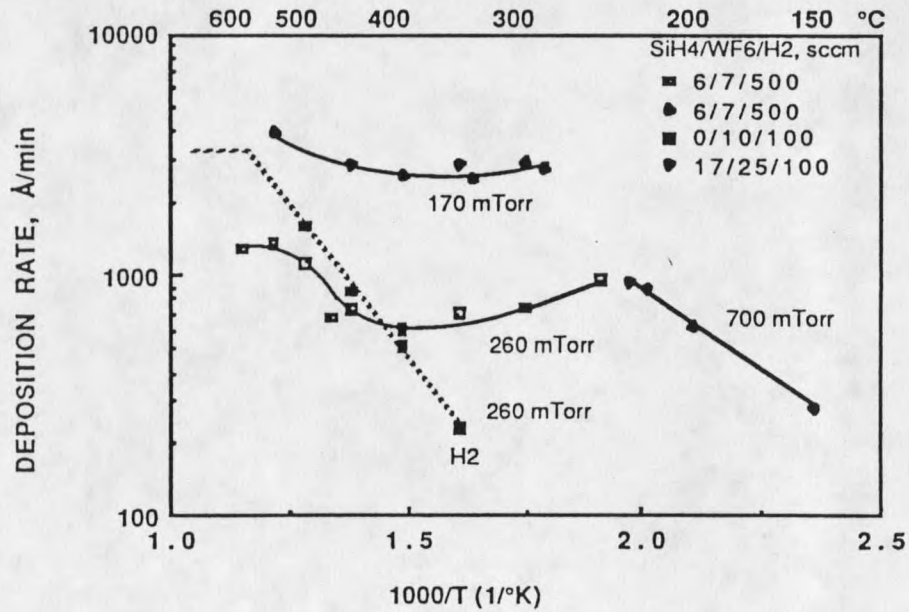


Figure 26. Arrhenius plot of blanket W deposition [10]. Comparison of H_2 and SiH_4 reduction. SiH_4 reduction at various flow rates and reactor pressures.

temperature range of 250-550°C, while the blanket W deposition rate was lower at low temperatures. They used a weight gain method to determine blanket deposit thicknesses, and SEM and step height measurements to determine selective W thicknesses in via holes. The Arrhenius plot for blanket deposition is given in Figure 26 and consisted of maxima and minima in a similar trend observed by Schmitz, et al. [9]. For a small temperature range between 150 and 200°C and at 0.7 torr, the activation energy was 0.28 eV/atom (26,780 Joule/mole). The rate expression was

$$R = k_0 e^{\frac{-E_a}{RT}} (P_{WF_6})^{-n} (P_{SiH_4})^1 \quad (22)$$

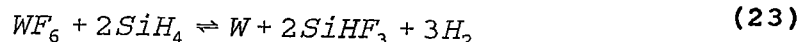
where, $n = 0-0.2$. They noticed that reactor pressure has an effect on the activation energy, and recommended that this effect be explored.

Ultra high vacuum (UHV) experiments by Yu, et al. [105] revealed that the reaction proceeds by repeating cycles of tungsten and silicon deposition. They used x-ray photoemission spectroscopy (XPS) to monitor the chemical species on the surface. The first cycle on the silicon surface is tungsten deposition through the reaction of WF_6 with silicon. Then, the deposition of silicon occurs by the reaction of SiH_4 with the fluorinated surface. Mass spectrometric studies showed that SiF_4 and H_2 are the major reaction products at low temperatures ($\sim 300^\circ C$). SiF_2 formation was observed at temperatures above $450^\circ C$ and HF formation at temperatures above $600^\circ C$. Since a

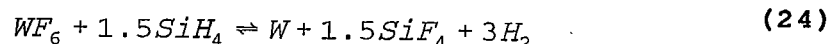
tungsten or a silicon seed layer on the substrate is the only requirement to start the tungsten deposition reaction with the $\text{SiH}_4\text{-WF}_6$ system, the substrate for the deposition is not restricted to silicon. Initial reactions of the $\text{WF}_6\text{-SiH}_4$ system with Al, PtSi and TiN surfaces have also been reported [106].

In another mass spectrometric analysis performed by Sivaram, et al. [107], it was confirmed that H_2 is the reaction product rather than HF for a Si/W ratio of less than 0.6 in the temperature range of 250-550°C. The absence of HF suggested that the SiH_4 decomposition results in molecular hydrogen (H_2), which desorbs without further reaction. The reaction was postulated to proceed by Si and H_2 formation on the surface and reaction of WF_6 with Si on the surface to form W. This is in agreement with the findings of Yu, et al. [104].

Kobayashi, et al. [108] used in situ Fourier transform infrared (FT-IR) spectroscopy and Auger electron spectroscopy (AES) to analyze the W formation reaction by the $\text{SiH}_4\text{-WF}_6$ reaction. They found that trifluoro-silane (SiHF_3), not SiF_4 , is the main by-product species, and proposed a new mechanism for the selective W deposition reaction. In a subsequent study, Kobayashi, et al. [109] introduced two reaction pathways and reported that by-product gases evolved during the reaction are a strong function of the SiH_4/WF_6 ratio. The proposed reaction pathways for the selective CVD region ($\text{SiH}_4/\text{WF}_6 < 1.0$) are



and



Reaction 23 was the dominant reaction for selective W-CVD on the silicon substrates.

Competitive adsorption of WF_6 and SiH_4 was believed to have an effect upon the reaction mechanism [104]. Growth rate versus WF_6 pressure profiles were supportive of this idea.

The initial stage of the tungsten formation reaction dictates the Si-W interface characteristics. Therefore, the electrical characteristics such as contact resistance and leakage current of a diffused layer are dependent on the initial reaction. Itoh, et al. [110] have analyzed the weight change versus deposition time data and speculated that there was a delay time at the initial stage of W deposition. Kajiyana, et al. [111] performed mass spectrometric analysis to evaluate the delay which occurs when SiH_4 is introduced into the reaction chamber as the first reactant. They related the delay time to the presence of the native oxide layer. NF_3 plasma treatment of Si surfaces removed the native oxide layer, and the delay time for nucleation was reduced.

Structural studies of CVD-W films with x-ray diffraction (XRD) analysis showed meta-stable β -W phase in addition to stable α -W and WSi_x phases. Reactions producing tungsten

silicide (WSi_x) are given in Table 1; their formation takes place at high SiH_4/WF_6 gas flow ratios.

Whereas β -W is a metastable phase of tungsten and is generally stabilized by the presence of impurity oxygen [112], α -W is a stable bcc tungsten phase [113]. The β -phase exhibits an A_3B (or A15) crystal structure [114], and the transformation of β -W to α -W is possible by heat treatment [115]. Table 2 contrasts α -W and β -W phases. Studies showed that β -W forms as a transition phase between α -W and WSi_x . Higher deposition temperatures and gas flow ratios of $\text{SiH}_4/\text{WF}_6 > 1.0$ resulted in β -W formation. Thermodynamic studies about the formation of W phases for SiH_4 - WF_6 reaction system are available in the literature [116,118].

Ohba, et al. [8] reported β -W formation when the SiH_4/WF_6 ratio was 4.0, and W_5Si_3 formation when the SiH_4/WF_6 ratio was 1.0 for temperatures above 380°C . Schmitz, et al. [104] observed α -W formation for $\text{SiH}_4/\text{WF}_6 < 1.3$, and β -W formation for $1.5 < \text{SiH}_4/\text{WF}_6 < 1.7$. Higher ratios yielded tungsten silicide deposition.

Tsutsumi, et al. [118] emphasized a critical value of the SiH_4/WF_6 ratio in order for the film structure to change from α -W to β -W. This value was between 0.4-1.0 and was dependent on the substrate materials examined (n^+Si , WSi_2 and TiSi_2).

The reactant ratio in the gas phase (SiH_4/WF_6) has an effect on the film morphology and impurity content. Tsutsumi, et al. [118] found that low SiH_4/WF_6 ratios delivered enough

Table 2. Tungsten Phases and Their Properties [114].

Phase	Structure	Lattice Constant, Å	Density, g/cm ³	Stability
α -W	bcc	3.165	19.3	stable
β -W	A15	5.036	19.1	metastable

lateral grain growth to form denser films, whereas high SiH_4/WF_6 ratios produced β -W films which contain larger amounts of oxygen and silicon. Ohba, et al. [119] have also found that the β -W films have higher impurity contents (e.g. F, O, Si) than do α -W films. Films of β -W exhibited porous structures and rough surfaces. Thus, β -W formation degraded the film conductivity. Nevertheless, overall, SiH_4 -reduced films were smoother than H_2 -reduced ones. Increasing temperatures and decreasing pressures produced smoother surfaces.

There have been studies to relate the resistivity to the impurity content of CVD-W films. Suzuki, et al. [120] used AES to analyze the Si content in the films. When Si concentration was less than 2 atomic %, Si dissolved substitutionally in α -W and the resistivity was proportional to Si concentration. When Si concentration was between 2-40 %, α -W and β -W were co-existent and the resistivity was not much affected by Si concentration. It was also speculated that Si segregates at the grain boundary of polycrystalline tungsten. Jeugd, et al. [121] employed AES and electron probe micro analysis (EPMA) to

elucidate resistivity dependence on the incorporated silicon. For $\text{SiH}_4/\text{WF}_6 = 1.0$, the increase in resistivity was $40 \mu\Omega\text{-cm/atomic \% Si}$. This was again explained by silicon segregation on the tungsten grain boundaries. On the contrary, Suzuki, et al. [122] stated that resistivity depends mostly on fluorine content, as determined by SIMS analysis, rather than silicon and oxygen content. Resistivity increased with increasing SiH_4 partial pressure and decreased with increasing temperatures down to $10 \mu\Omega\text{-cm}$ at 330°C . Ohba, et al. [119] reported that resistivity can be as low as $8 \mu\Omega\text{-cm}$ for W formed at 400°C (similar to the value obtained by H_2 reduction). This confirms Rosler's finding of $7.5\text{-}8.5 \mu\Omega\text{-cm}$ for deposition temperatures above 400°C [10].

Orientation of deposited films is another factor to be considered for kinetic evaluations. X-ray diffraction patterns in some research papers showed a (110) preferred orientation of tungsten crystals when $\alpha\text{-W}$ was the dominant phase [7,8,120]. In contradiction to these, Schmitz, et al. [9] reported a dominant (100) orientation for both $\text{H}_2\text{-WF}_6$ and $\text{SiH}_4\text{-WF}_6$ systems. Film orientation may be a result of deposition kinetics and/or be a cause in influencing the deposition kinetics of the subsequent layers. So far, no significant deliberation of this parameter has been available in the literature on W films formed from the $\text{SiH}_4\text{-WF}_6$ reaction.

A high film quality for VLSI technology requires that films have low stress values and have good adhesion to the

substrate. This is essential for a reliable device performance over a long period of time. Almost all films deposited are found to be in a state of internal stress regardless of the deposition method. The stress may be compressive or tensile [13]. The total stress in a film is the sum of: (a) the external stress on the film, usually from another film; (b) the thermal stress, resulting from the difference in the coefficients of thermal expansion between the film and the substrate; and (c) the intrinsic stress, which originates from the changes in the film structure. Saitoh, et al. [123] have reported that SiH_4 -reduced, CVD-W films have higher stress than do H_2 -reduced films. Ohba and Inoue [124] analyzed the stress for selectively deposited tungsten films. The film stress was a function of both deposition temperature and film thickness. When the wafers were heated from the back side, the stress changed from tensile to compressive as the deposition temperature and the film thickness increased. They observed that peeling occurred for the films deposited at low temperatures. This was in agreement with Rosler, et al. [10] since they reported excellent adhesion of W to Si at temperatures above 350°C .

CHAPTER 3

EXPERIMENTAL

Reaction SystemEquipment

A schematic diagram of the low pressure chemical vapor deposition (LPCVD) reaction system is given in Figure 27. Because of the hazardous characteristics of the gases used, the system is placed in a hood. The main parts of the system are: the gas lines and controllers, the reactor, the pressure controller, the pumps, the effluent gas treatment system, and the oil filtering system.

Gas Lines and Controllers: The gases used for the experiments are semiconductor-grade tungsten hexafluoride (WF_6), semiconductor-purity silane (SiH_4), and U.H.P. purity argon (Ar) as carrier gas. Specifications of the gases are given in Table 3; characteristics of the reaction gases and their hazards and handling are given in Appendix A. The tungsten hexafluoride line is kept heated to around $40^\circ C$ to reduce the possibility of condensation.

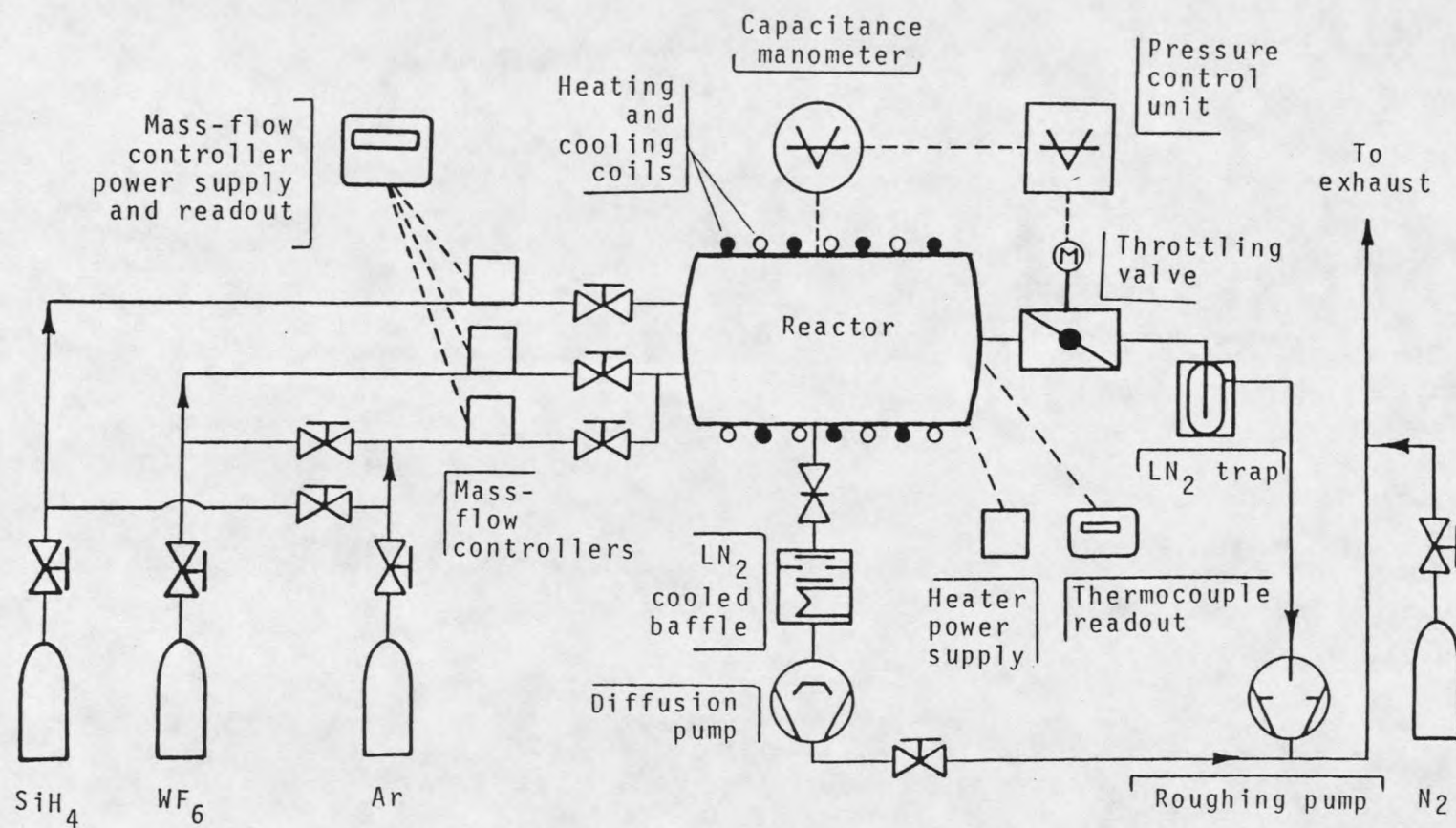


Figure 27. Schematic diagram of the LPCVD reaction system.

Table 3. Specifications of the Reaction Gases.

Gases	Component Specifications	
Tungsten hexafluoride (WF_6)	$\text{Ar} \ \& \ \text{O}_2 < 10 \text{ ppm}$	$\text{CO}_2 < 5 \text{ ppm}$
	$\text{HF} < 1,000 \text{ ppm}$	$\text{SiF}_4 < 10 \text{ ppm}$
	$\text{SF}_6 < 10 \text{ ppm}$	$\text{N}_2 < 10 \text{ ppm}$
	$\text{CF}_4 < 10 \text{ ppm}$	
Silane (SiH_4)	$\text{Ar} \ \& \ \text{O}_2 < 2 \text{ ppm}$	$\text{N}_2 < 2 \text{ ppm}$
	$\text{CH}_4 < 0.2 \text{ ppm}$	$\text{CO} < 1 \text{ ppm}$
	$\text{H}_2\text{O} < 1 \text{ ppm}$	$\text{CO}_2 < 1 \text{ ppm}$
	$\text{SiCl}_x < 1 \text{ ppm}$	
Argon (Ar)	$\text{O}_2 < 1 \text{ ppm}$	$\text{THC} < 0.2 \text{ ppm}$
	$\text{H}_2\text{O} < 1 \text{ ppm}$	

Three MKS type 1259 mass flow controllers and an MKS 247B four-channel readout and power supply unit are used to control the inlet gas flow rates. The controllable operation range for mass flow controllers are 0-120 sccm (standard cubic centimeters per minute) for tungsten hexafluoride, 0-305 sccm for silane, and 0-200 sccm for argon.

Reactor: The reactor system is a 6-way cross stainless steel vacuum chamber approximately 1.5 liters in volume. The reactor walls are wrapped with heating tapes and cooling coils

for bake-out and cold-wall reactor options, respectively. Figure 28 shows a cross-sectional view of the reactor.

The reactor is accessed by a flange on which the sample heater is attached. The sample heater is a copper block 6.3x6.3x1.3 cm in dimension with cartridge heaters. Silicon wafers are mounted on the block surface with screws from the wafer edges to ensure good conductive heating. Three 200-watt cartridge heaters, 7.6 cm in length and 0.95 cm in diameter, are inserted into the holes in the copper block assuring a good thermal contact. These cartridge heaters are connected in series and powered by a manually controlled 220-V variac.

Wafer temperature is measured by a 1/16 inch chromel (Type K) sheathed thermocouple mounted on the sample heater just beneath the wafer. This temperature is checked against a bare thermocouple placed on the copper block adjacent to the silicon wafer. These two readings agree within a 10°C temperature difference. It is observed that the calibration of the bare thermocouple changes during the reaction as the deposited tungsten layer on the junction point changes the thermocouple characteristics. Therefore, the sheathed thermocouple reading is taken as the reference for the experiments and corrected temperatures for the surface are reported.

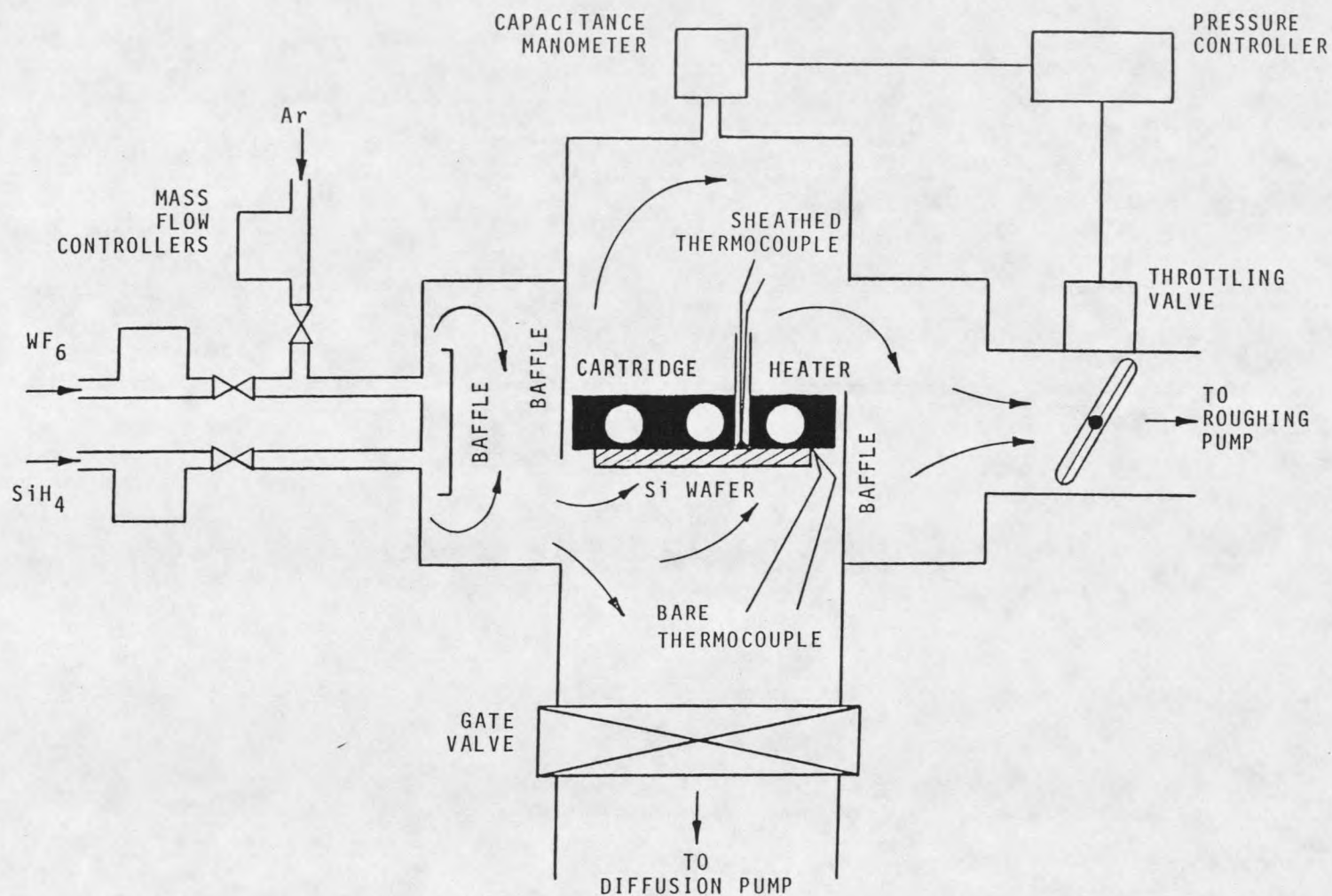


Figure 28. Cross-sectional view of the LPCVD reactor (substrate horizontal).

Pressure Controller: The reactor pressure is measured by a Type 12A MKS Baratron Vacuum Gauge. The readings are in terms of absolute pressures and the gauge has a range of 0.001-10 torr. The gauge is connected to an MKS PDR-D-1 Power Supply and Digital Readout unit. The system pressure is automatically regulated by an MKS Throttling Valve Type 253A-1-1-40-1. The throttling valve is a butterfly valve and is placed on the pumping line after the reactor. Pressure is regulated by varying the valve opening which in turn varies the pumping speed seen by the chamber. The throttling valve is powered and controlled by an MKS Type 252A Exhaust Valve Controller.

Pumps: The LPCVD system consists of one roughing pump and one diffusion pump.

The roughing pump is a Varian SD-300 Standard Series Mechanical Pump with two-stage direct drive. It has 310 l/min free air displacement and can deliver a vacuum of better than 10^{-4} torr. The pump is designed to provide vibration-free operation and is equipped with an anti-suckback valve to prevent oil from being sucked back into the vacuum system should the motor be stopped inadvertently. The pump is operated with Varian GP Type General Purpose Mechanical Pump Fluid.

A CVC-M60 diffusion pump is used for bake-out. The pump is air cooled and can pump down the system to 10^{-7} torr. A

liquid nitrogen-cooled baffle is placed between the diffusion pump and the chamber to prevent oil backstreaming into the chamber. Between the reaction chamber and the liquid nitrogen trap is a gate valve Model SVB-2.5V14, Torr Vacuum Products Inc. Varian Neovac SY Diffusion Pump Fluid is used in the pump.

Effluent Gas Treatment: The pyrophoric and corrosive natures of the reactant and product gases require special treatment before being purged into the exhaust hood. The treatment is carried out in two steps.

The first step is the condensation of reactor effluent gases by passing them through a liquid nitrogen trap, which is placed right after the throttling valve. The trap consists of a stainless steel cylinder, 10 cm in diameter and 20 cm in height, and is immersed in a liquid nitrogen container. The gas inlet and outlet pipes are 5 cm in diameter and are attached to the top flange. The inlet pipe goes inside the cylinder about 15 cm to require the gas to traverse a longer path inside the trap. The unreacted reactant and product gases except for H_2 and Ar condense at the liquid nitrogen temperature. This condensation action, in effect, serves as a cryopump, further increasing the pumping speed.

The second step is simply nitrogen dilution of gases right before the purge. Nitrogen gas is added to dilute the stream approximately 100 times at the roughing pump outlet.

Oil Filtering System: WF_6 forms hydrogen fluoride and a variety of tungsten oxides upon exposure to air. Tungsten oxide particles inside the roughing pump cause failure in the vanes. Thus, a continuous filtering and neutralization of the pump oil is necessary (Oil filtering system is not shown in Figure 27).

Some of the roughing pump oil is pumped by a MR1-23-49SM Simplex Milroyal Pump (a reciprocating, positive-displacement pump) to a Carquest Oil Filter 85050. The filter can retain particles as small as $10\text{ }\mu\text{m}$. The filtered oil is then sent to a neutralizer to remove the acidic fluorides. The neutralizer is a stainless steel cylinder 860 cm^3 in volume and is packed with Akzo Chemie Ketjen Catalyst, Silica-alumina ($SiO_2-Al_2O_3$) HA5P. The neutralized oil is passed through a rotameter, which also serves as a sight glass, and recycled back to the roughing pump. The pressure at the recycling pump outlet is continually monitored to make sure that the filter is not plugged. The filter and neutralizer packing is changed when the oil becomes darker.

Experimental Procedure

Sample Preparation

Before each experiment, reactor walls are wiped clean with methanol-dampened tissue.

One quarter of a 10-cm diameter (100) oriented boron- or phosphorus-doped silicon wafer is first washed with methanol to remove any organic residue on the surface. After rinsing with distilled water, the wafer is dipped in diluted 100:1 HF solution for 1 minute to eliminate the native oxide layer before the deposition. Elimination of the oxide layer is evidenced by a change in the attachment characteristics of distilled water on the silicon surface. Upon the elimination of the oxide layer, water has less tendency to attach to the silicon surface. The final cleaning is done with acetone and methanol wash. The cleaned wafer is then positioned on the substrate heater and is mounted in the reactor. Si substrates are positioned either vertically facing the reactor inlet or horizontally facing downward. In the vertical case, the baffles on both sides of the sample heater are removed (not shown in Figure 28).

Deposition

Reactor Preparation: After placing the sample in the reactor, initial pumpdown is done through the roughing line. When a vacuum better than 0.1 Torr is reached, the throttling

valve is closed and the chamber is pumped down through the diffusion pump line. The system is baked out at around 1×10^{-7} Torr for 60-90 minutes to remove the water vapor from the system. The bake-out temperature for the substrate and the reactor walls are $\sim 500^\circ\text{C}$ and $\sim 150^\circ\text{C}$, respectively. At the end of bake-out, the system is allowed to cool down to reaction conditions. Cooling of the reactor walls is facilitated by running water through the cooling coils.

After the cool-down, the gate valve is closed and the argon valve is opened for partial back-filling of the chamber. When the system pressure reaches about 0.1 Torr, argon flow is discontinued. The throttling valve is then opened to pump down the system through the roughing line. An increase in the system pressure before opening the throttling valve is necessary to prevent any back diffusion from the roughing line.

Before the reaction, the liquid nitrogen trap is filled, and time allowed for the temperature measured at the trap flange to drop to about -15°C . The substrate temperature and the system pressure are stabilized under argon flow. Meanwhile, the reactor walls are maintained at about 60°C to minimize WF_6 condensation which in turn may cause reactant depletion for the substrate.

Reactor Operation: After stabilization, SiH_4 and WF_6 are introduced into the chamber simultaneously and a chronograph is started. During the reaction, the substrate temperature is controlled manually through a variac to within $\pm 3^\circ\text{C}$. The reaction times vary from 0.5 minutes to 12 minutes. At the end of the reaction, the SiH_4 and WF_6 valves are manually closed at the same time, the throttling valve is completely opened, and the chronograph is stopped. The system is purged with argon for about 1 minute, then the argon valve is closed. During the argon purge, cooling water for the reactor walls is turned on to minimize any possible desorption of gases from the reactor walls and their subsequent adsorption on the substrate which could cause further reaction.

The substrate temperature is decreased at a rate lower than $5^\circ\text{C}/\text{min}$. Such a low rate does not impose high temperature gradients across the deposited W-Si interface that would contribute to delamination of the W layer (especially when the adhesion is poor). Under these conditions, the sample is allowed to cool below 45°C . The chamber is then filled with argon to atmospheric pressure, and the sample is taken out.

Data Analysis

For data evaluation, sheet resistance measurements, gravimetric measurements, SEM, XRD, and AES are used. Consistency in sampling is maintained by taking the samples

from similar locations on wafers for each analysis (e.g. from the center of the wafer for film thickness measurements).

Sheet Resistance Measurement

The sheet resistance values are directly measured by a 4-point probe. Measurements are performed on the whole one-quarter of wafer used for the deposition. The ranges of voltage and current used in measurements are 10-100 μV and 0.1-0.8 mA, respectively. During the measurements, the voltage is kept low so as not to induce local heating which could cause an increase in resistivity. The uniformity of the W film thickness is checked by performing sheet resistivity measurements at different locations on the wafer (one in the center and four on locations approximately 1 cm away from the edges of the wafer). All the measurements are taken at room temperature. Before proceeding with the rest of analysis, 1-cm wide blocks are cut off from the sides of wafers to minimize end effects.

Film Thickness Measurement

After the sheet resistance measurements, two samples, approximately 1.0x1.0 cm in dimension, are cut from the center of the wafer and weighed on a CAHN 29 Automatic Electrobalance. Then, the deposited tungsten layer is dissolved in 0.25M KH_2PO_4 / 0.24M KOH / 0.1M $\text{K}_3\text{Fe}(\text{CN})_6$ solution. It is necessary to heat the solution to boiling in

order to attain a reasonable etching rate. At the end of etching, samples are washed with distilled water, rinsed with acetone and dried prior to weighing. Successive etching and weighing processes are carried out until there is no significant change in weight. The total weight of the samples, depending on the size, varies in the range of 60-180 mg, while the weight loss is 0.2-19 mg. The electrobalance is sensitive to 1 μg weight difference in the working range of 1-250 mg. A Smiec Dial Caliper is used for area measurements. The caliper is sensitive to 0.00254 cm (0.001 in). The roughly rectangular samples are measured on each side and the average value for each opposing side is recorded. The area is then calculated assuming each sample to be a perfect rectangle. Knowing the area, A , and the weight loss after etching, Δm , tungsten film thickness, δ , is found from the formula

$$\delta = \frac{\Delta m}{\rho_b A} \quad (17)$$

A constant bulk density, ρ_b , of 19.3 g/cm is assumed throughout the calculations.

SEM Analysis

Samples for SEM analysis are cut to 0.3x1-cm dimension and are mounted on copper sample holder boats with a graphite adhesive solution. A JEOL-100CX Electron microscope with a scanning attachment equipped with ASID-4D is used for the analyses. The system has a lateral resolution of 30 Å. Plan-

view micrographs are taken at 20 keV primary beam energies and at 10,000x and 40,000x magnifications. Cross-sectional micrographs are taken at Applied Materials, Santa Clara, California. A 6,000x magnification is used.

AES Analysis

The AES surface analysis and depth profiling are carried out with a Physical Electronics, PHI 595 Scanning Auger Microprobe. The minimum electron beam size for the probe is 500 Å. The depth profiling is performed by rastering a 2x2 mm area for 30-second intervals. The argon (Ar^+) ion beam current and voltage for sputtering is $\sim 150 \mu\text{A}/\text{cm}^2$ and 3 kV, respectively. The primary electron beam voltage used is 3 keV with an accompanying beam current of $0.2 \mu\text{A}$. The data acquisition is achieved by a DEC PDP 11/04 computer. The sensitivity factors used for surface concentration analysis are given in Table 4 [125].

Table 4. AES Sensitivity Factors [125].

Si = 0.35	W = 0.055	O = 0.52
C = 0.2	F = 0.49	

X-ray Diffraction Analysis

X-ray diffraction analysis is performed on a General Electric XRD-5 diffractometer. X-ray source is Ni-filtered $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) operated at 45 kV and 18 mA. Beam widths for the beam and detector slit widths are 1° and 0.2° , respectively. Medium range collimating assemblies are used for both the incident and reflected beams. Scanning speed of the Goniometer is $2^\circ 2\theta/\text{min}$ and chart speed is 1 in/min, giving a $2^\circ 2\theta/\text{in}$ diffractogram scale for the samples. Tungsten deposited Si wafers are scanned through a 2θ range of $30\text{--}80^\circ$. An approximate sample size of $2 \times 2 \text{ cm}$ is required for the analysis.

Scope of the Experiments

The SiH_4/WF_6 ratio, R , is kept constant throughout the experiments at 1.0 to favor $\alpha\text{-W}$ deposition over $\beta\text{-W}$ and tungsten silicide (WSi_x) deposition. The flow conditions for reactant gases are given in Table 5. "Horizontal" and "vertical" substrate positions are used in the experiments. The "horizontal" substrate position is shown in Figure 28 wherein the Si substrate faces downward, parallel to the overall flow across the chamber. The second baffle after the reactant entrance diverts the course of reactant gases toward the lower part of the chamber. The third baffle forces the reactants upward in the reactor where they can react on the Si

substrate surface. The reactant and product gases then leave from the upper chamber. In the case of the "vertical" substrate position, the substrate in Figure 28 is rotated 90° clockwise to face the reactant inlet. The second and the third baffles are removed. The "vertical" substrate position is therefore perpendicular to gas flow. The temperature and pressure dependence of the WF_6 - SiH_4 reaction and W films are analyzed in two parts:

(1) The first set of the experiments is designed to establish kinetic parameters while covering a temperature range as wide as possible ($\Delta T = \sim 250^\circ C$).

Substrate position : Horizontal, facing downward.

Reaction time : 4 minutes.

Temperature : 137-385°C.

Pressure : 1, 3, 10 torr.

(2) The second set of experiments is primarily designed to examine tungsten crystal growth trends with time, but also to evaluate the effect of substrate position on the kinetic parameters.

Substrate position : Vertical, facing reactant entrance.

Reaction time : 0.5-12 minutes.

Temperature : 285-385°C.

Pressure : 1, 10 torr.

Table 5. Gas Flow Conditions.

Substrate position	P (torr)	WF ₆ (sccm)	SiH ₄ (sccm)	Ar (sccm)
Horizontal	10	120	120	70
	3	110	110	64
	1	110	110	64
Vertical	10	110	110	64
	1	110	110	64

CHAPTER 4

RESULTS

The experimental results will be presented in six main sections. The first introduces the preliminary experiments for kinetic studies. The second presents the AES analysis findings on the impurity content of deposited films. The third includes the gravimetric analysis of the reaction rate and establishes the Arrhenius plot for the WF_6 - SiH_4 system. The fourth presents the SEM analysis of tungsten crystal morphology and growth patterns. The fifth reports x-ray diffraction analysis of tungsten phases and crystal orientation. The sixth explains the tungsten film resistivity in relation to film structure.

Preliminary Experiments

Reaction rates for tungsten deposition were found from the mass deposited at a corresponding reaction time using the gravimetric method. Equivalent film thickness was calculated from Equation 17. The calculations do not give the actual film thickness unless the film density is known. The method is suitable as far as kinetic studies and Arrhenius activation analysis are concerned since it directly gives the amount of tungsten formed. The resolution of the electrobalance used in weight measurements was 0.001 mg. The area of the chip samples

analyzed for W deposition was approximately 1 cm^2 . Therefore, when a constant W bulk density of 19.3 g/cm^3 is assumed, the equivalent thickness for continuous films could be predicted within $\pm 5 \text{ \AA}$. Deposition rate was found from the average thickness of W deposits. Two $1.0 \times 1.0 \text{ cm}$ Si chips were taken from the center of each wafer and an average film thickness was calculated. Average deviation in the rate was $\pm 10\%$ (maximum of $\pm 33\%$) for the horizontal substrate position and $\pm 6\%$ (maximum of $\pm 12\%$) for the vertical substrate position.

The expected effect of reactant gas flow rate on the deposition rate is discussed in Chapter 2. Prior to the final experiments on reaction kinetics, a set of experiments was conducted to find the flow rates of reactants for which the kinetics are free of starvation or mass flow rate limitations. These results are shown in Figure 29. The highest temperature, 385°C , for the project study range, which would give the highest deposition rate, was utilized. The flow rate for the kinetic studies was chosen from the region in which the deposition rate is independent of the flow rates. Gas flow rates for the horizontal substrate position were $\text{WF}_6 = \text{SiH}_4 = 120 \text{ sccm}$, $\text{Ar} = 70 \text{ sccm}$ for 10 torr total reaction pressure; $\text{WF}_6 = \text{SiH}_4 = 110 \text{ sccm}$, $\text{Ar} = 64 \text{ sccm}$ for 1 and 3 torr total reaction pressure. The reactor system has a limited pumping capacity; consequently, flow rates chosen for 3 and 1 torr

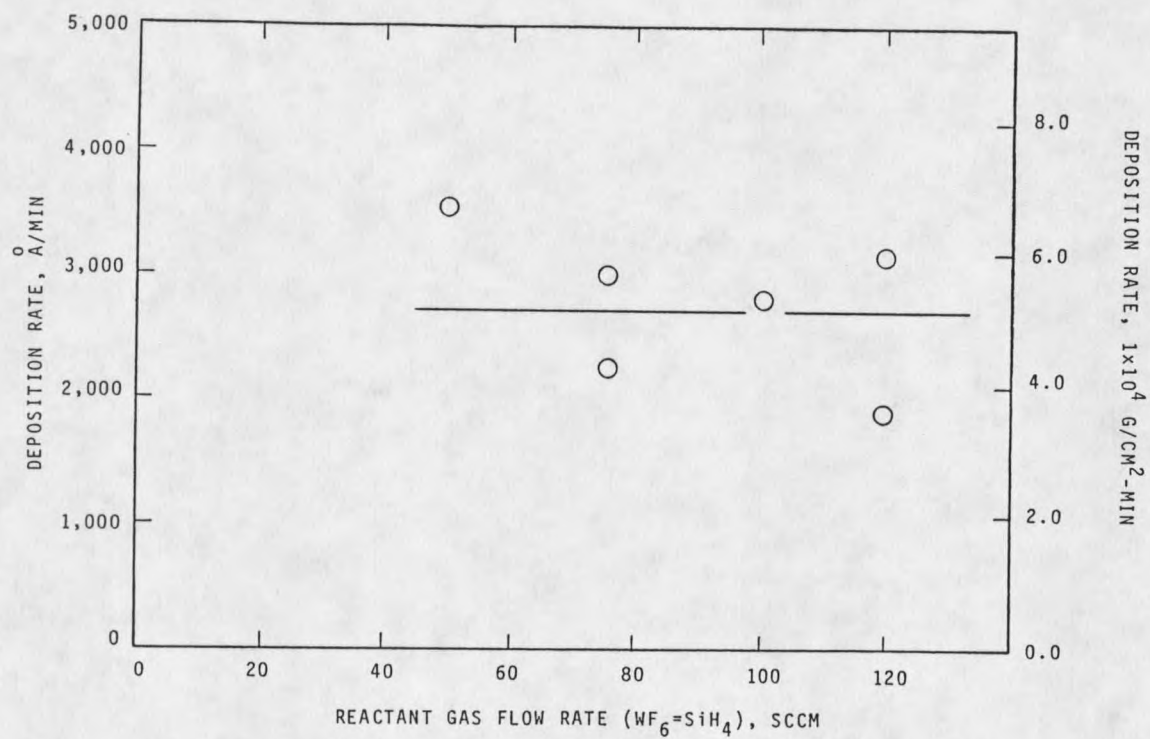


Figure 29. Preliminary experiments to assure differential reactor. (Horizontal substrate position, $P = 10$ torr, $T = 385^{\circ}\text{C}.$)

were lower than those for 10 Torr in order to attain the desired low pressures. Gas flow rates for the vertical position were constant for both 1 and 10 torr ($WF_6 = SiH_4 = 110$ sccm, Ar = 64 sccm).

Selectivite deposition of W on Si was tested by using 1.0 x 1.0-cm patterned wafers with 3500 Å oxide layers on the silicon. These wafers were placed next to Si(100) wafers on the substrate block. Tungsten deposition on both Si and SiO_2 (i.e. blanket W deposition) was observed within the experimental range studied.

AES Analysis

Impurity content of tungsten films was analyzed by Auger electron spectroscopy (AES). Possible atomic impurities are oxygen (O) from air, carbon (C) from CO or CO_2 from air and from back diffusion of pump oil, fluorine (F) from unreacted WF_6 or from undesorbed reaction products such as SiF_x or HF, and silicon (Si) from decomposition of SiH_4 or from undesorbed SiF_x . Si may also be present in the films as a result of silicide formation.

Auger depth profiles for tungsten films deposited at 10 torr-137°C, 1 torr-137°C, and 3 torr-385°C are given in Figures 30, 31, and 32, respectively. These samples are representatives of different deposition temperatures and presesures. The AES curves are from the samples with 4-minute

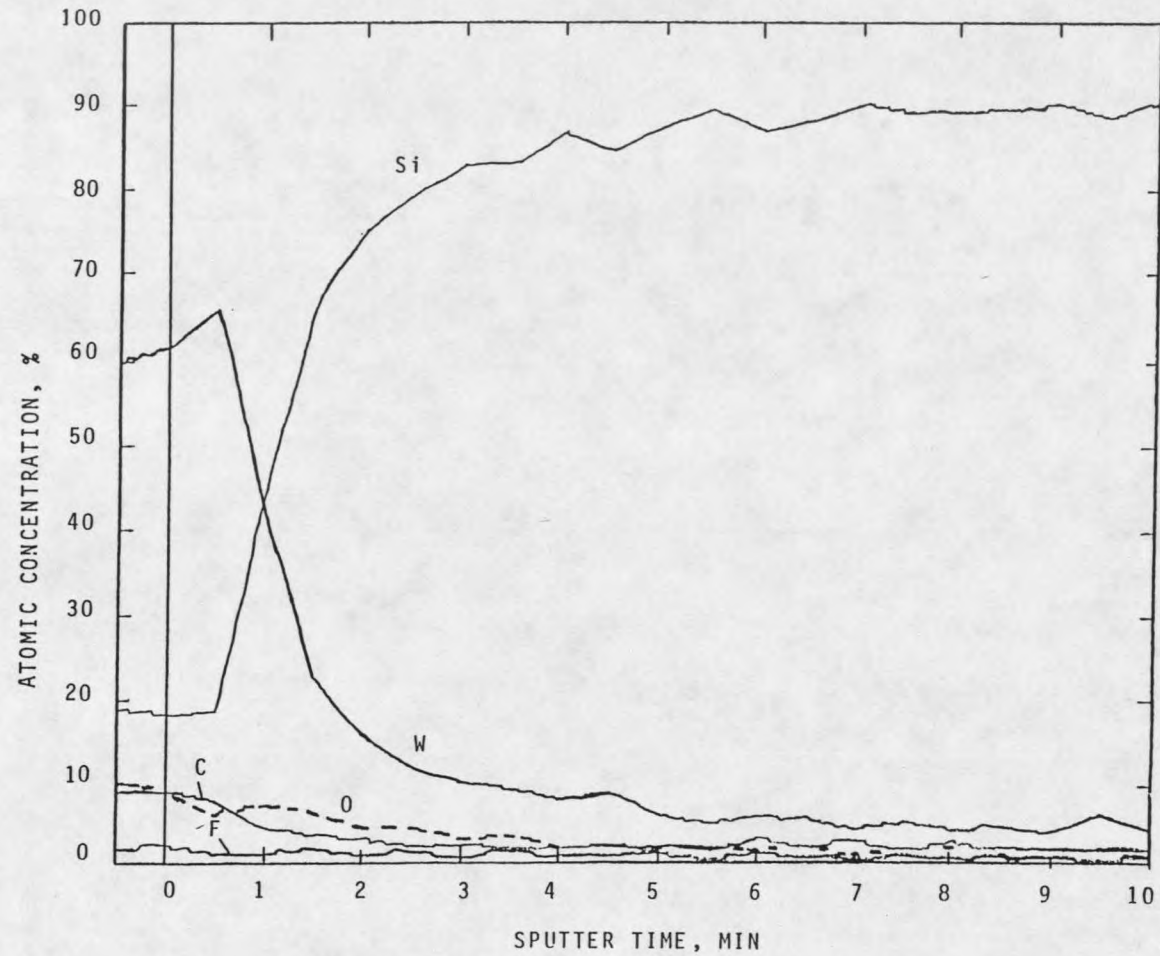


Figure 30. Auger depth profile for W film deposited at 10 torr and 137°C (t=4 min).

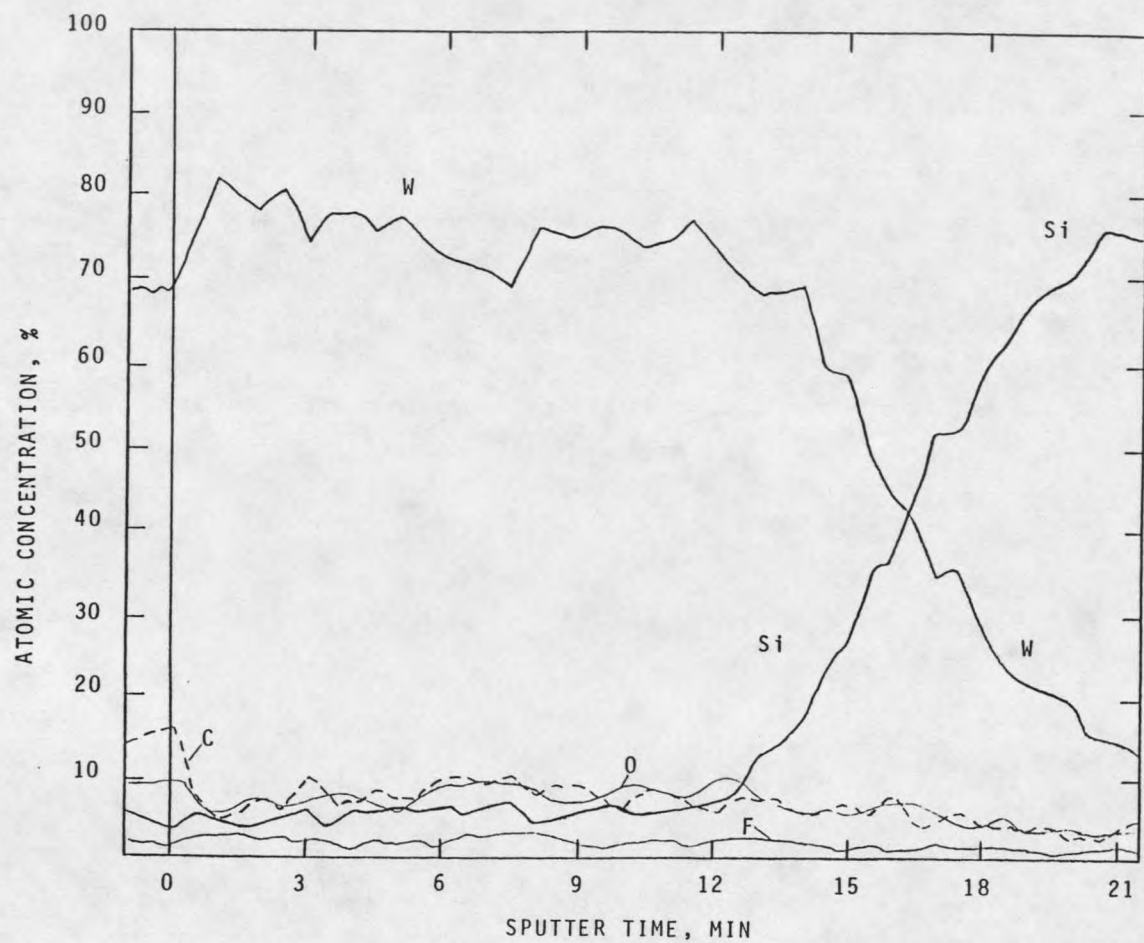


Figure 31. Auger depth profile for W film deposited at 1 torr and 137°C (t=4min).

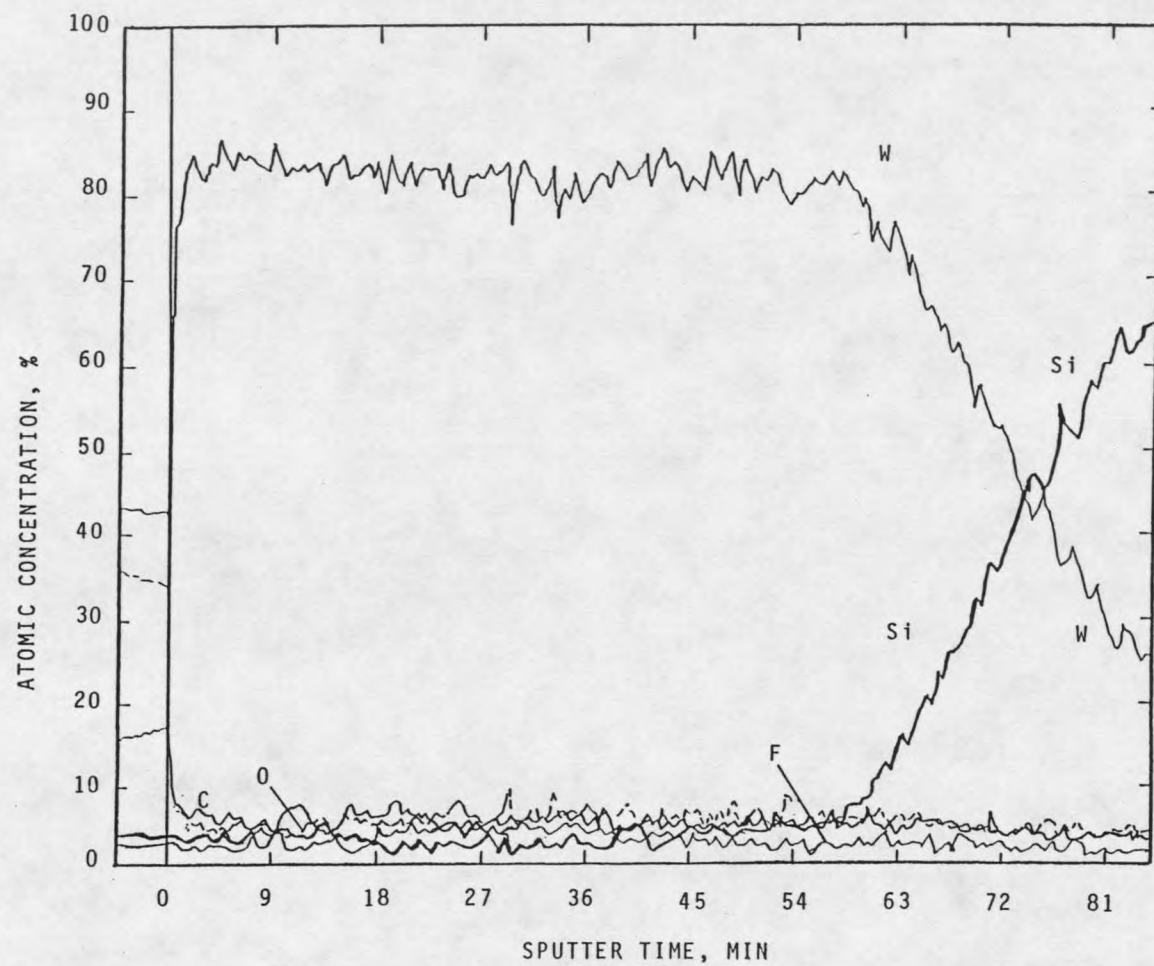


Figure 32. Auger depth profile for W film deposited at 3 torr and 385°C (t=4min).

reaction times. The Si-W interface is reached at longer sputter times for thicker films. Impurity contents in these films were within the noise level for Auger detection which was confirmed by a detailed analysis of the differential Auger spectra. Other analysis techniques, such as neutron activation analysis (NAA), electron probe micro analysis (EPMA), and secondary ion mass spectroscopy (SIMS) analysis are required to conclusively support the AES findings. However, there are no significant changes in atomic impurity concentrations throughout the film thicknesses. Another implication is that the low Si concentrations (practically in the noise level) excludes the presence of tungsten silicides in the films. Thus, the confirmed existence of only one reaction, tungsten formation, justifies one to proceed with the kinetic analysis of this particular reaction.

Other samples examined by AES depth profiling exhibited similar patterns. As explained in the SEM analysis section, the film deposited at 10 torr-137°C (Figure 30) was very thin and had a non-uniform W concentration distribution on the surface. Non-uniformity in W surface concentration was determined by observing different W concentrations on different locations on the surface by Auger analysis. High concentration sites probably correspond to initial nucleation sites implying that the film is primarily in the nucleation stage with minor surface diffusion under these reaction conditions.

Kinetics-Gravimetric

The thickness of the deposited tungsten ranged from 300 to 88,000 Å. The Arrhenius plot for $\text{SiH}_4\text{-WF}_6$ reaction system is given in Figure 33. The data correspond to 4-minute reaction times. It is quite striking to see that the apparent activation energy changes with system pressure, which is contrary to the $\text{WF}_6\text{-H}_2$ system [5]. The apparent activation energies are 0.35 eV/atom (33,300 J/mole) for 10 torr, 0.17 eV/atom (16,600 J/mole) for 3 torr, and 0.08 eV/atom (7,800 J/mole) for 1 torr. Different activation energy values for different pressures indicate that the rate controlling mechanism changes with pressure. The data presented in Figure 33 are for the horizontal sample position (substrate surface facing downward). Similar activation energy behavior was also observed in Figure 34 with sample in the vertical position (facing the reactant inlet). The data for 1- and 1.5-min reaction times are presented in Figure 34. The results for 0.5-min reaction time have been determined to be not suitable for kinetic studies and are excluded. The reason is that it takes approximately 15-20 seconds for the system pressure to stabilize after the introduction of reactants, thus a 30-second reaction time is far from representing a steady state reactor operation. Activation energies presented in Figure 34 are for the films which are still in the island/coalescence stage. The vertical substrate position yielded higher

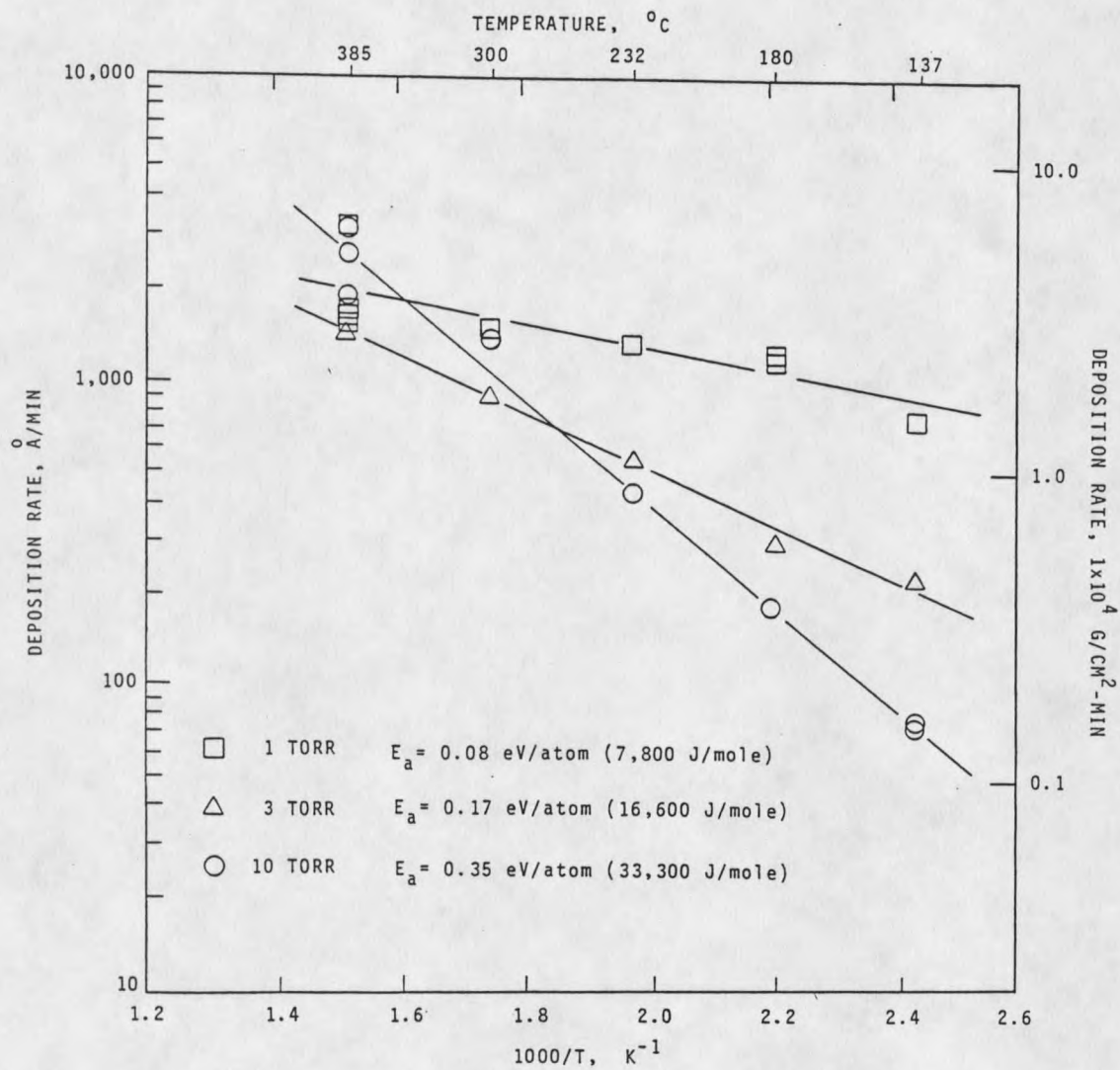


Figure 33. Arrhenius plot for $\text{WF}_6\text{-SiH}_4$ system. Substrate horizontal, $t = 4$ min.

activation energies than did the horizontal substrate position. The apparent activation energies for the vertical position are: 0.40 eV/atom (38,300 J/mole) for 10 torr, and 0.12 eV/atom (11,420 J/mole) for 1 torr. The average rates for longer reaction times (10-12 minutes) are shown also. Dashed lines in Figure 34 are provided as visual aids only, they do not represent a fit for data. Note that 10 to 12-minute reaction times correspond to a rate for continuous film formation where reaction surface area and crystal orientation are different from those of the island/continuous film stage. Evidently, the deposition rate changes with film thickness. This is discussed together with SEM and XRD analysis results later.

SEM Analysis

Experiments for SEM analysis were conducted in two parts: time-dependent experiments for kinetic studies and experiments to form thick films for morphological studies. Additionally, the original experiments with tungsten films grown for 4 minutes were analyzed by SEM.

Time-dependent Experiments

A set of reaction-time-dependent experiments was performed to analyze the crystal growth habits. Individual aggregate sizes were measured by using SEM plan-view

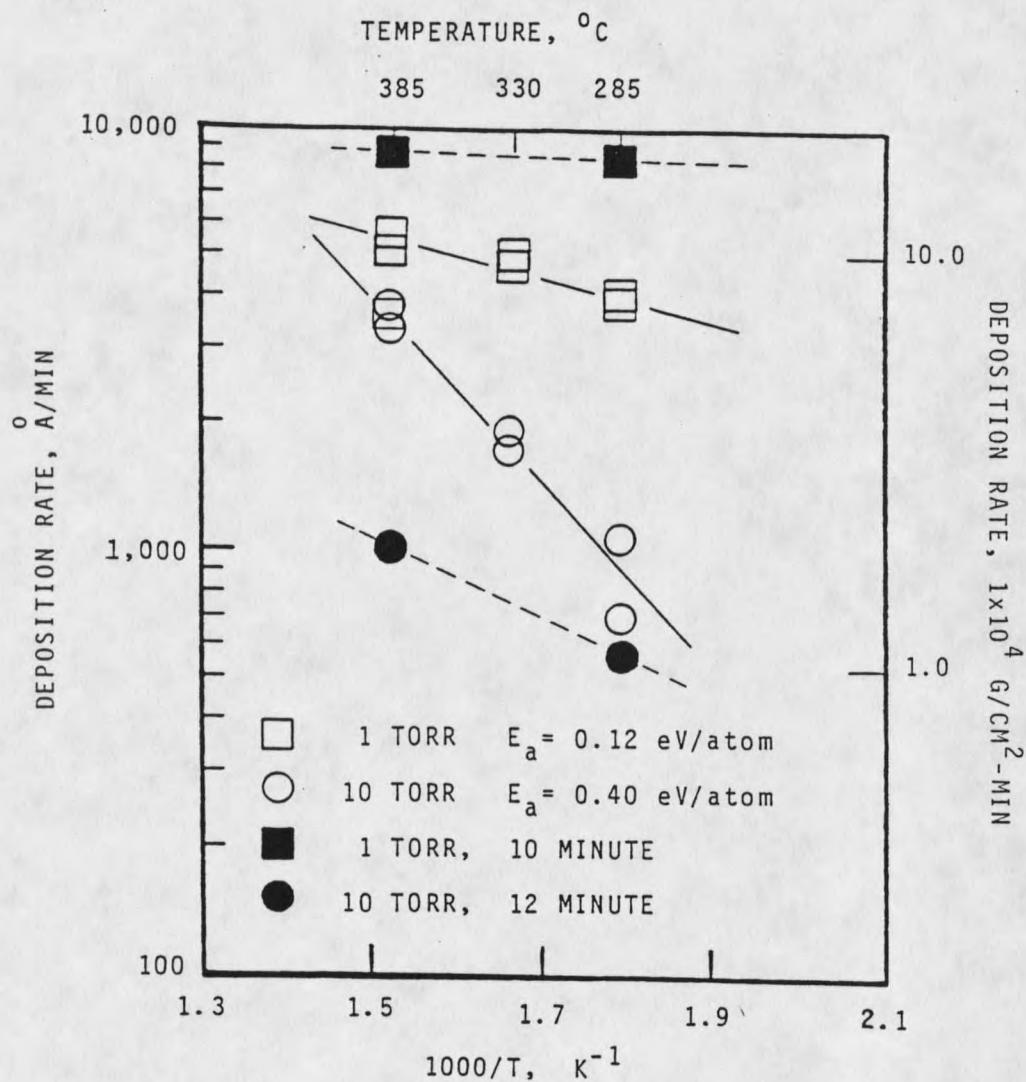


Figure 34. Arrhenius plot for $\text{WF}_6\text{-SiH}_4$ system. Substrate vertical; ○ and □ $t = 1\text{-}1.5$ min, ● and ■ $t = 10\text{-}12$ min.

micrographs of tungsten surfaces. An average aggregate size was determined for each deposition condition.

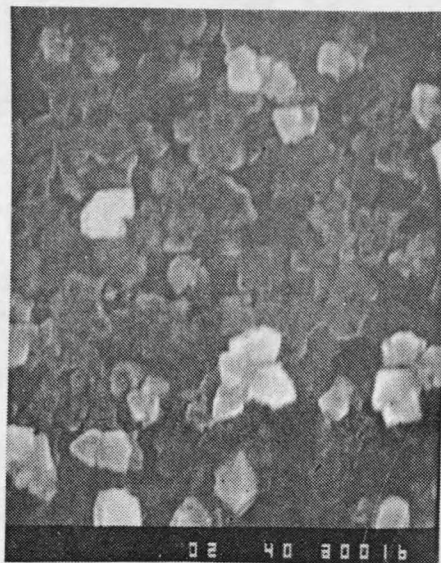
Figure 35 shows how the aggregates grow with time for the deposition condition of 10 torr and 385°C. At 0.5 min, islands have already formed and some of them have grown vertically more than the others. This stage shows very limited lateral growth. At 1.0 min, aggregates are bigger and they show more crystalline structure with sharper geometries. The film appears highly porous. At 12 min, aggregates have had enough time to grow and touch each other. A complete coalescence at the 12-min deposition time is not observed; however, porosity appears lower than that at smaller deposition times.

Figures 36 and 37 show tungsten film surfaces deposited at temperatures of 285, 330 and 385°C for 1.5 minutes at 10 torr and 1 torr, respectively. Aggregate sizes for 1 torr are larger than those for 10 torr. This is a result of higher deposition rates at lower pressures. Within 1.5 minutes under the reaction conditions the tungsten surfaces are still in the island/coalescence stage except for the film deposited at 1 torr-385°C (The deposition rate at this condition was high enough to form a continuous film in 1.5 min). The complete set of SEM micrographs for the time dependent experiments are included in Appendix H.

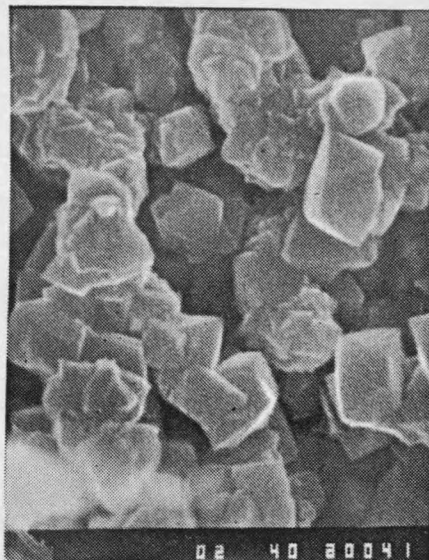
Average aggregate size versus reaction time data are presented in Figures 38 and 39 for 10 torr and 1 torr, respectively. The average aggregate sizes for reaction

$P=10\text{ Torr}$, $T=385\text{ }^{\circ}\text{C}$

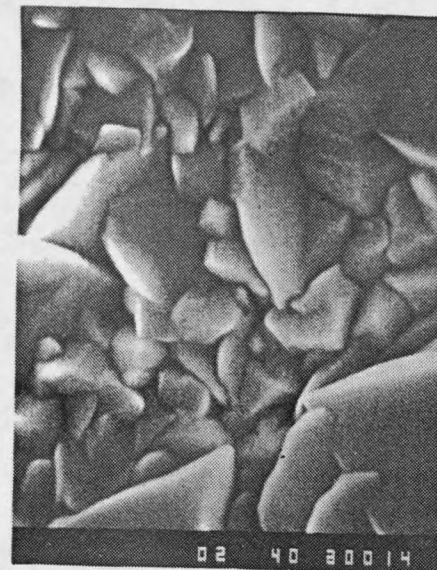
————— $1\mu\text{m}$



$t = 0.5\text{ min}$



$t = 1.0\text{ min}$



$t = 12\text{ min}$

Figure 35. SEM micrographs of W surfaces at different reaction times.

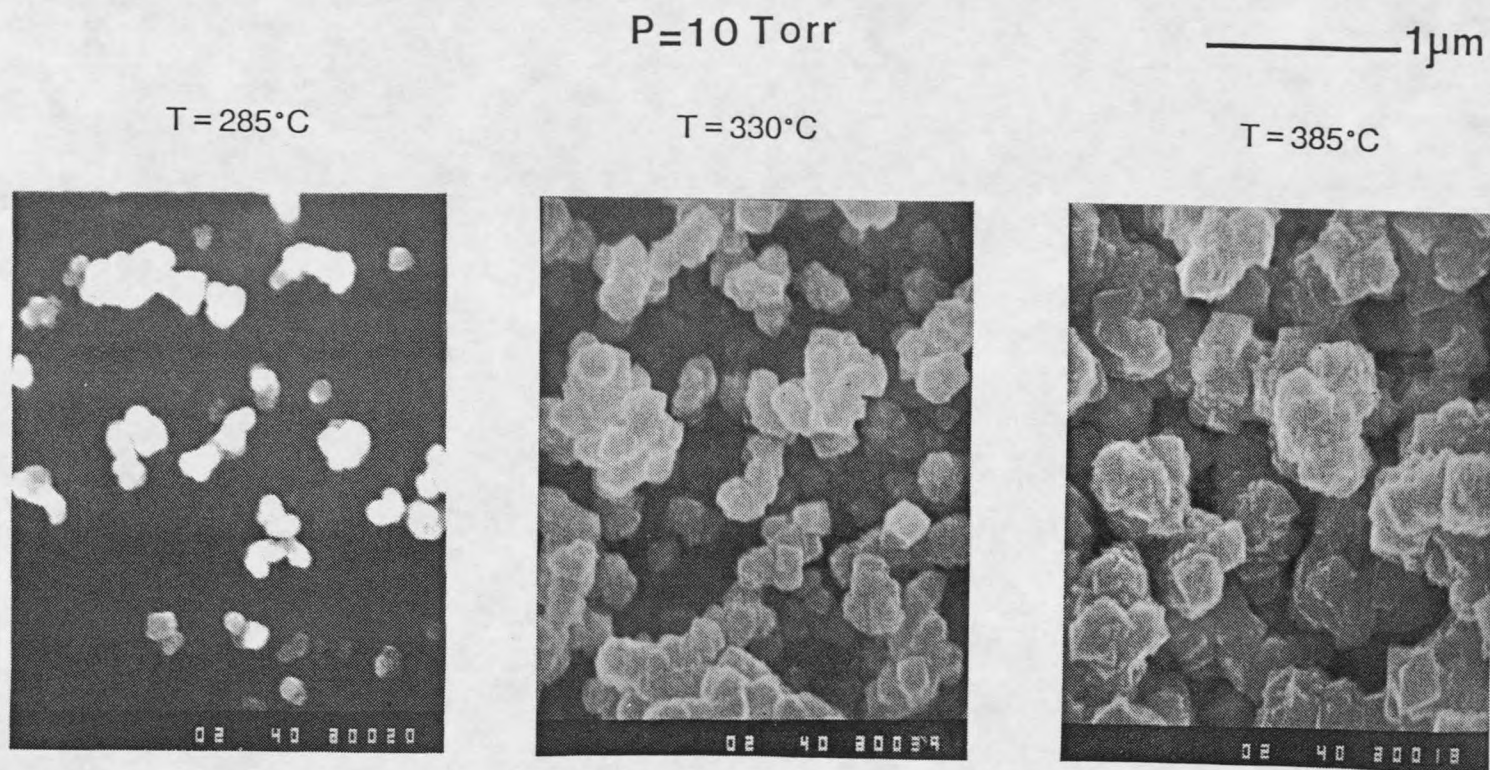


Figure 36. SEM micrographs of W surfaces , $t = 1.5 \text{ min}$, $P = 10 \text{ torr}$.

_____ 1 μm

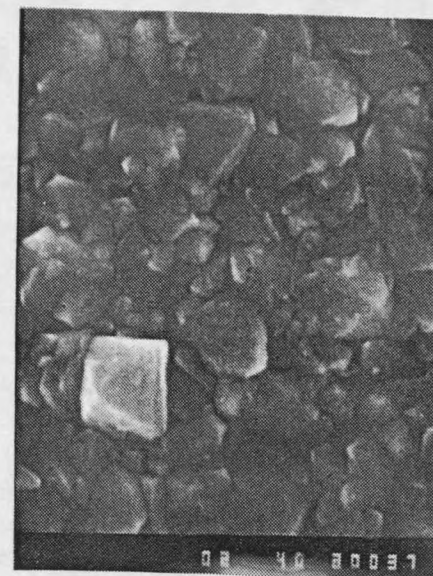
$$T = 385^{\circ}\text{C}$$


Figure 37. SEM micrographs of W surfaces, $t = 1.5$ min, $P = 1$ torr.

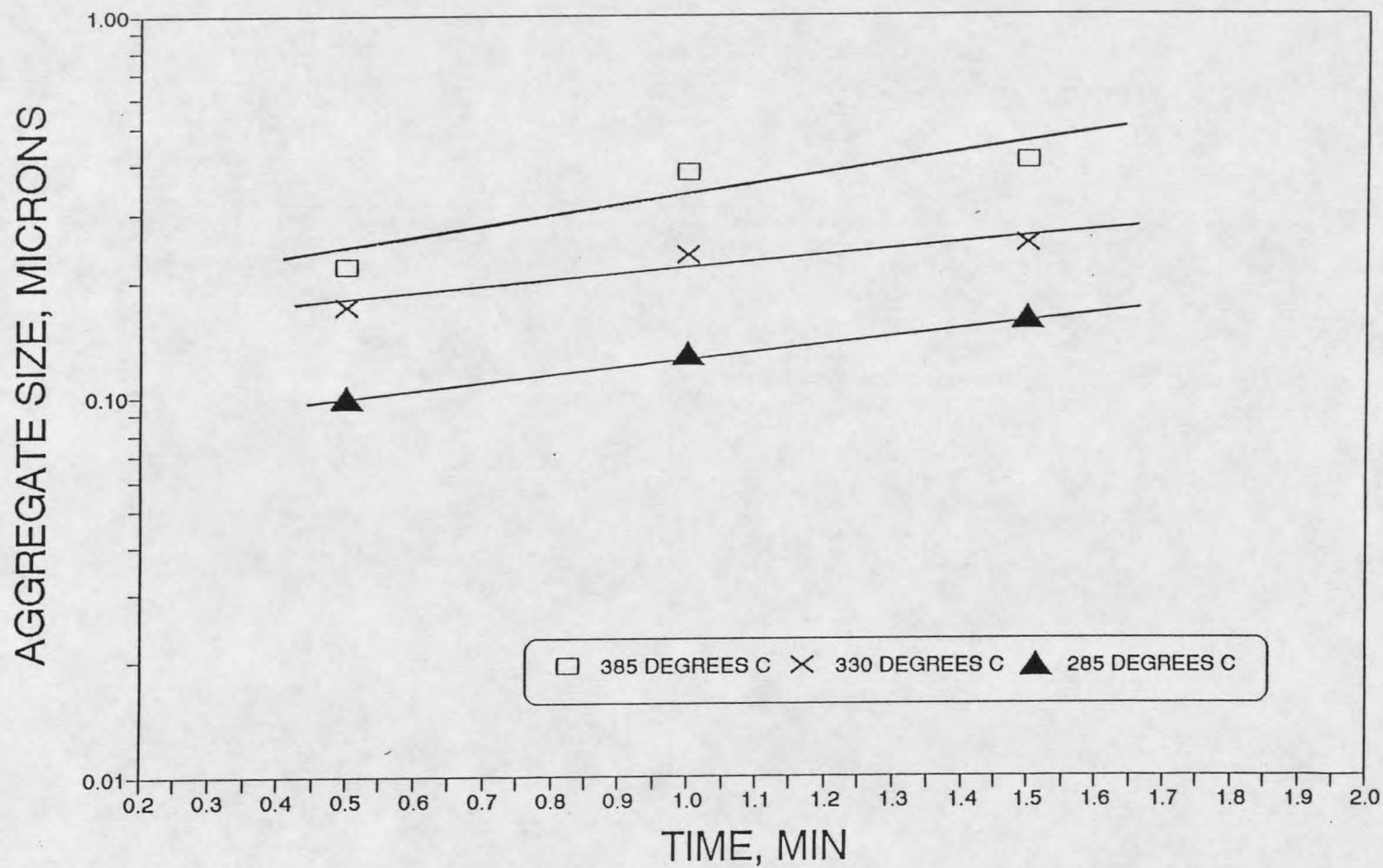


Figure 38. Aggregate growth rate, parallel to surface, P = 10 torr.

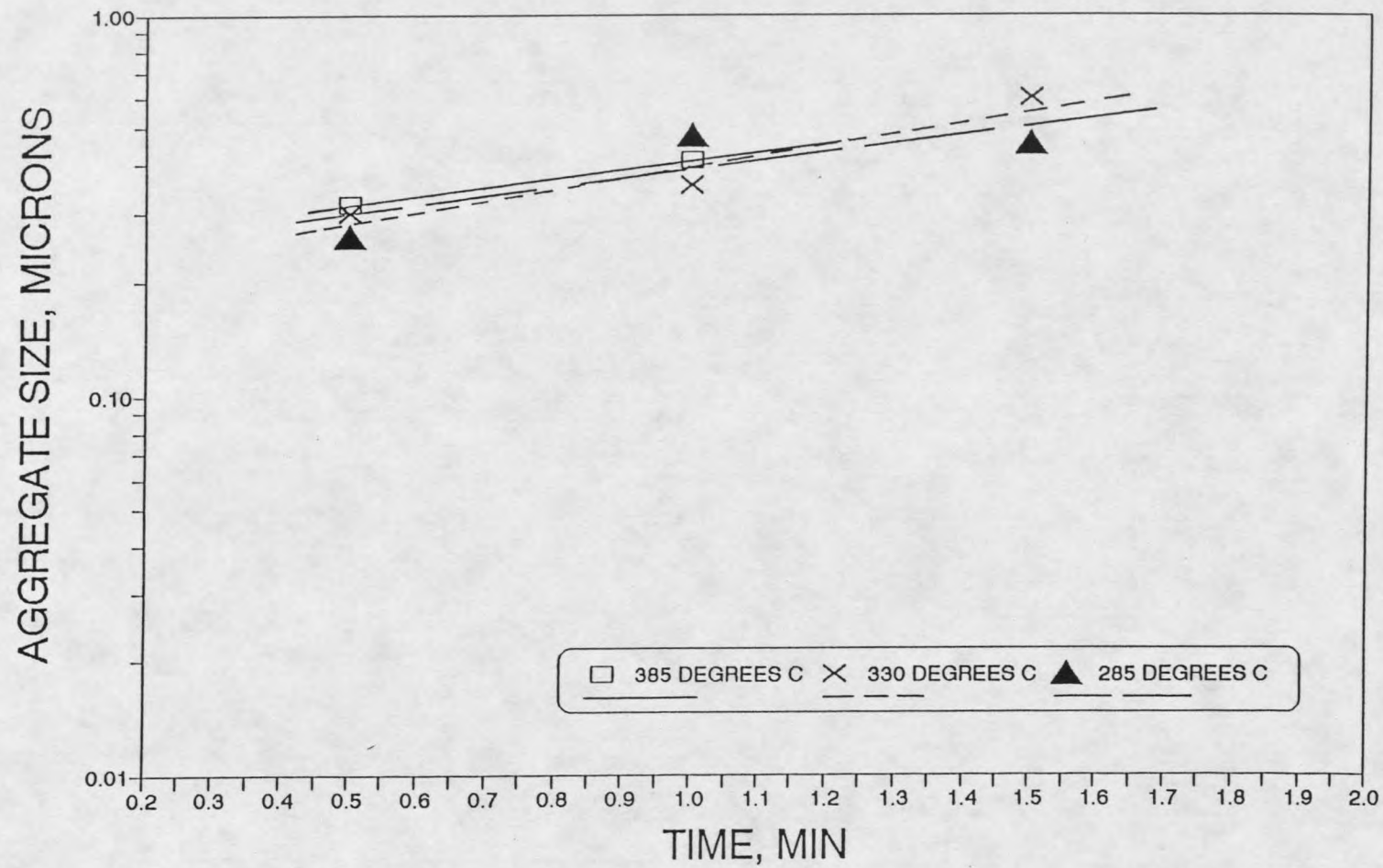


Figure 39. Aggregate growth rate, parallel to surface, P = 1 torr.

pressures of 1 torr are larger than those for 10 torr when the deposition time and temperature are the same. The slope of the aggregate size versus reaction time curve for each temperature was used to calculate the aggregate growth rate. The calculated aggregate growth rates reflect growth parallel to silicon surface only. At 10 torr, aggregate size increases with increasing temperature, while at 1 torr it is almost insensitive to temperature.

The aggregate growth rates found from Figures 38 and 39 were used to prepare an Arrhenius plot for crystal growth parallel to surface which is presented in Figure 40. The values of activation energies calculated from these graphs do not have much statistical significance but one can at least determine the trends. The Arrhenius plots show the same relative dependence on pressure as observed with the gravimetric method (10 torr vs. 1 torr in Figures 33 and 34). The absolute values for the parallel aggregate growth activation energies are 0.09 eV/atom (9,080 J/mole) for 10 torr, and 0.009 eV/atom (865 J/atom) for 1 torr.

Overgrown Films

The change in crystal morphology and orientation as a function of reaction temperature and pressure was analyzed by growing thick tungsten films. Film thickness varied from 1.6 to 8.7 μm . Reaction times were 12 minutes for 10-torr experiments and 10 minutes for 1-torr experiments. SEM plan-

view micrographs are presented in Figures 41 and 42, and SEM cross-sectional micrographs in Figures 43 and 44.

At 10 torr-285°C the film is still porous (Figures 41,43) indicating a 3-dimensional growth, where the growth in the vertical direction is faster than that in the horizontal direction. This implies a growth mode mostly controlled by gas phase impingement rather than surface diffusion. At 10 torr-385°C, the film is less porous, crystals touch each other, and crystallographic shapes are more definite.

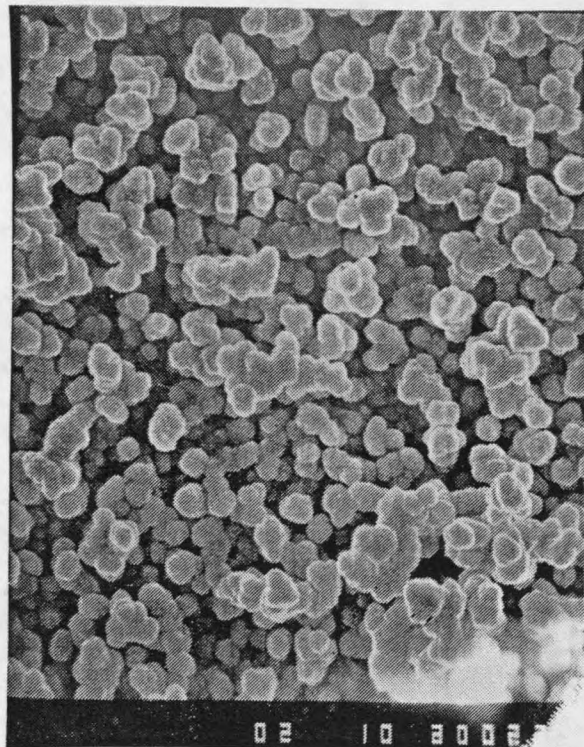
At 1 torr, films exhibit a continuous structure indicating a coalescence phenomena. For 285°C, the interface shows a porous structure (Figure 44). The cross-sectional view implies that after a certain height from the interface, some nuclei grow relatively faster, precluding others from growing. These fast-growing nuclei then coalesce and yield a continuous film. At 385°C, the tungsten film shows a columnar growth starting immediately from the substrate interface. The film is continuous without porous zones, and the thickness is quite uniform.

4-Minute Experiments

Surface morphology of tungsten films deposited during the 4-minute experiments, for the samples positioned horizontally, was also examined by SEM. The tungsten surfaces formed at different pressures are shown in Figures 45 and 46 for deposition temperatures of 385°C and 137°C, respectively. In

$P=10$ Torr

$T=285^{\circ}\text{C}$



$T=385^{\circ}\text{C}$

$1\mu\text{m}$

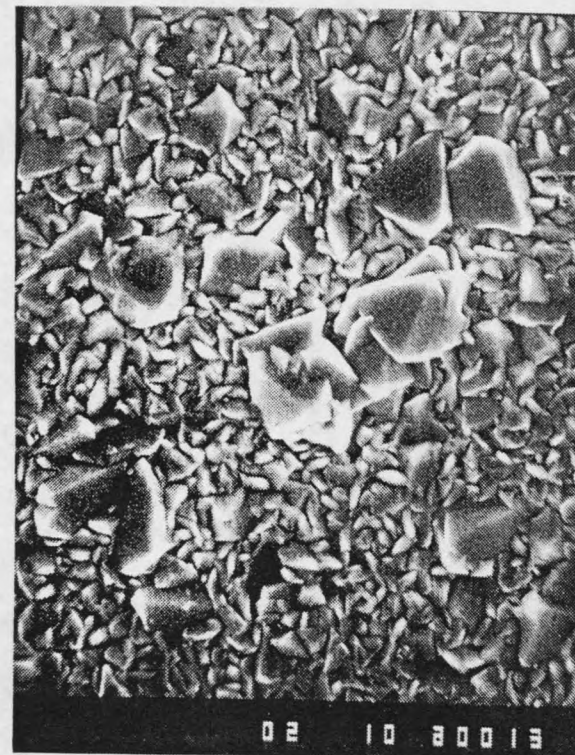
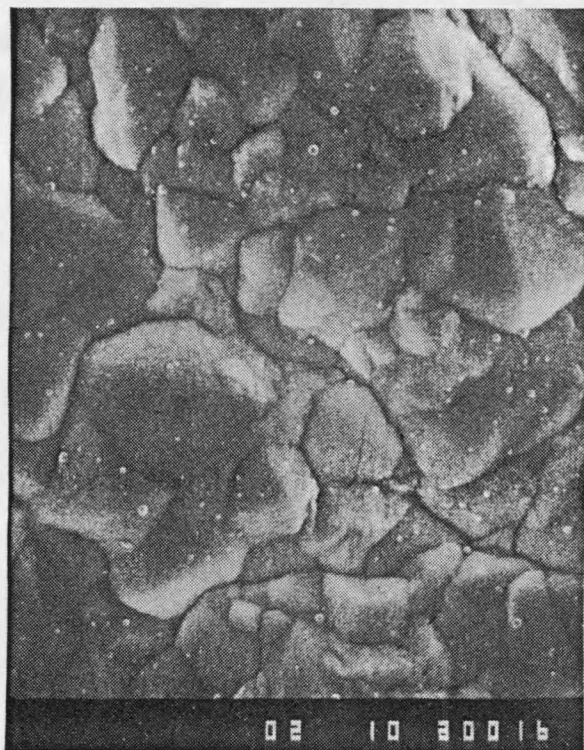


Figure 41. SEM micrographs of tungsten surfaces, $t = 12$ min.

$P = 1 \text{ Torr}$

$T = 285^\circ\text{C}$



$T = 385^\circ\text{C}$

$1 \mu\text{m}$

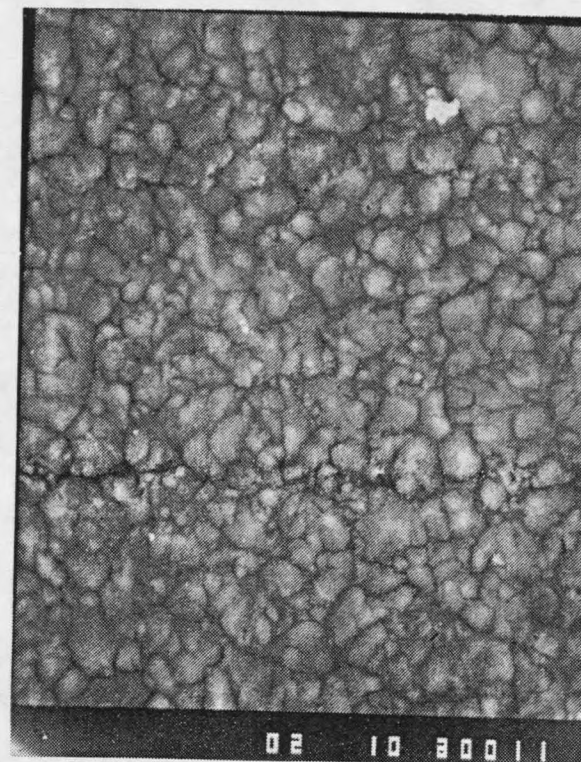


Figure 42. SEM micrographs of tungsten surfaces, $t = 10 \text{ min}$.

$P=10$ Torr

$T=285^{\circ}\text{C}$

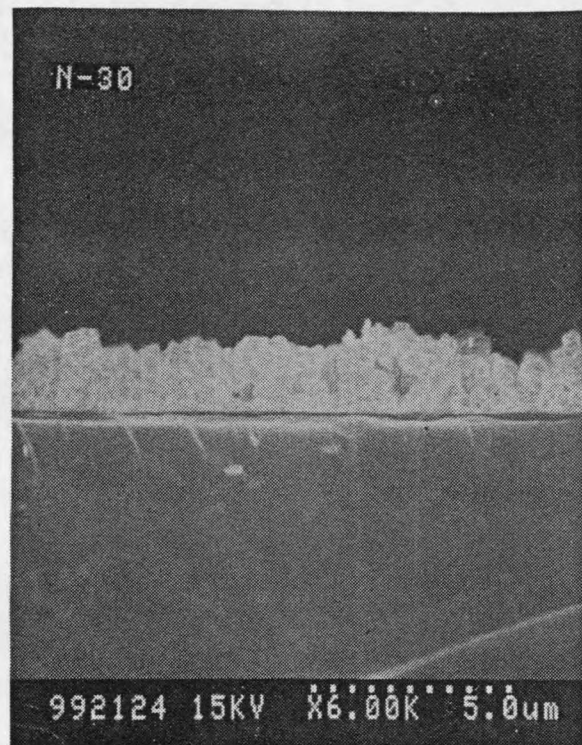
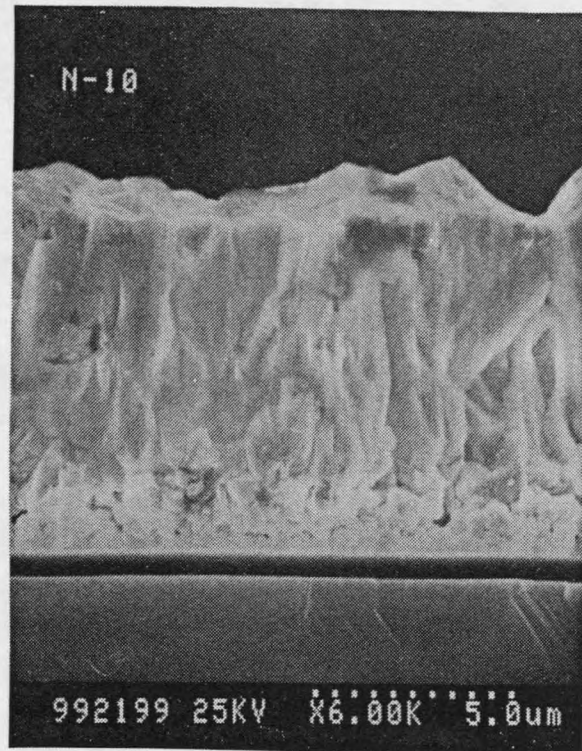


Figure 43. SEM cross-sectional view of tungsten film, $t = 12$ min.

$P = 1 \text{ Torr}$

$T = 285^\circ\text{C}$



$T = 385^\circ\text{C}$

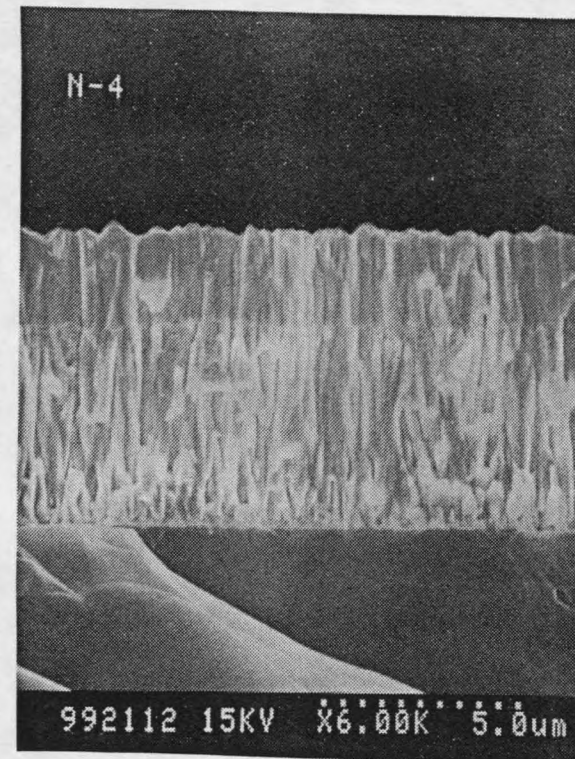
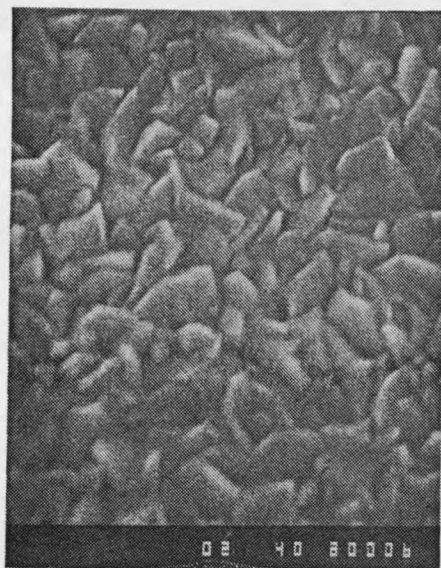


Figure 44. SEM cross-sectional views of tungsten films, $t = 10 \text{ min.}$

P=10 Torr



P=3 Torr



—————1 μ m
P=1 Torr

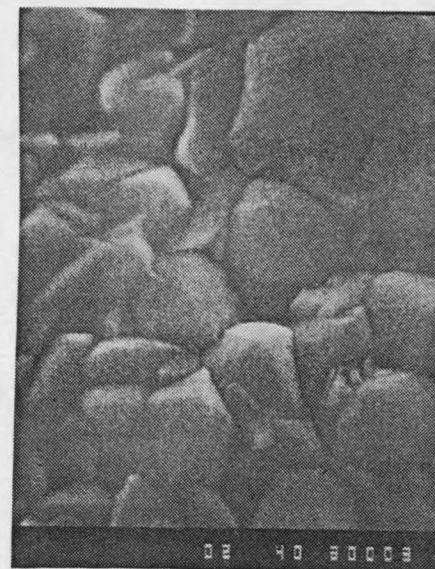


Figure 45. SEM surface micrographs of W deposited at 385°C ($t = 4\text{min}$).

P=10 Torr



P=3 Torr



—————1 μ m
P=1 Torr



Figure 46. SEM surface micrographs of W deposited at 137°C ($t = 4$ min).

both figures, lower pressures and higher temperatures yield larger-sized crystal aggregates. Higher temperatures give more definite crystal structures (Figure 45 vs. Figure 46).

At 137°C-10 torr (Figure 46), the deposition rate is the lowest, and tungsten islands are barely observable. However, at 137°C-1 torr, the aggregate sizes are bigger and a continuous film is already formed. Adhesion was a significant problem for thick, low temperature deposits (lower than 300°C). The combined effect of poor adhesion and relatively high stress developed cracks and lifting in the films. A typical crack is seen in Figure 46 for 1 torr. Some films had such a low adhesion that film peeling was observed after a minor physical contact with these films.

X-ray Diffraction Analysis

The types of phases and orientation of tungsten crystals formed by the deposition reaction were examined by x-ray diffraction analysis. The range examined for 2θ was between 30° and 80°, wide enough to identify α -W, β -W, and tungsten silicide (WSi_x) phases. Diffraction angles for these phases for various crystal orientations are given in Appendix F. These values were used for the identification of tungsten films.

The highest and the lowest deposition temperatures and pressures were chosen for x-ray diffraction analysis. For each deposition condition, two samples at different film

thicknesses (different reaction times) were analyzed. Figure 47 shows x-ray diffraction patterns of tungsten films deposited at 285°C and 10 torr for 1.5-minute and 10-minute reaction times, respectively. The spectra clearly indicate an α -W deposition. Only a few samples were found to contain trace amount of β -W. However, $\text{CuK}\beta$ radiation ($\lambda = 1.49 \text{ \AA}$) was also present in the x-ray source ($\text{CuK}\alpha_1$, $\lambda = 1.54 \text{ \AA}$) to give satellite peaks as labeled on the figure. Figure 47 reveals a typical trend of a change in crystal orientation with thickness. Thinner films, or shorter reaction times, show an α -W(110) domination, whereas for thicker films, or longer reaction times, this domination is attenuated in favor of the α -W(200) orientation. Intensity values normalized for thickness for each main α -W orientation are given in Table 6 for shorter and longer reaction times. Intensities were established from peak heights. The switch from (110) orientation to (200) orientation with increasing reaction time and therefore film thicknesses is seen most obviously for 1 torr reaction conditions where the deposition rates and corresponding thicknesses are relatively high. Thinner films exhibit an orientation close to the random orientation reported in the X-ray Powder Data File [33]. The bottom row in each table gives the per cent intensities calculated from the X-ray Powder Data File. Calculations were performed to convert relative intensities into normalized values (per cent

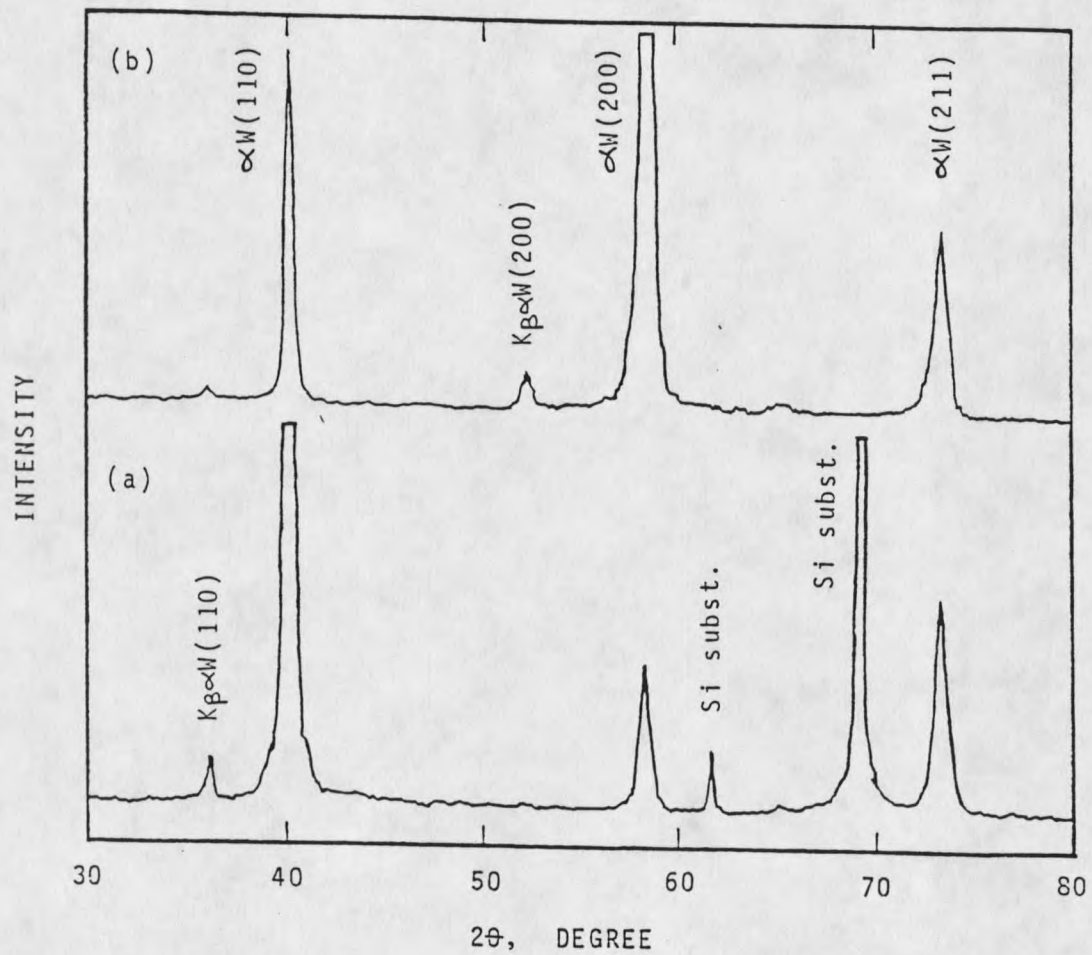


Figure 47. X-ray diffraction patterns of W films deposited at $T = 285^\circ\text{C}$ and $P = 1$ torr:
(a) $t = 0.5$ min, (b) $t = 10$ min.

Table 6. X-ray Diffraction Intensities of Tungsten Films.

		% INTENSITY					
		285°C			385°C		
		α -W(110)	α -W(200)	α -W(211)	α -W(110)	α -W(200)	α -W(211)
10 TORR	1.5 MIN	82	9	9	81	8	11
	12 MIN	79	9	12	69	18	13
1 TORR	0.5 MIN	78	9	13	64	25	11
	10 MIN	25	62	13	1.5	98	0.5
POWDER DIFFRACTION		72	11	17	72	11	17

Table 7. X-ray Diffraction Peak Widths of Tungsten Films.

		FWHM*, 1×10^{-4} radians					
		285°C			385°C		
		α -W(110)	α -W(200)	α -W(211)	α -W(110)	α -W(200)	α -W(211)
10 TORR	1.5 MIN	106	140	237	68	103	95
	12 MIN	56	88	116	53	66	78
1 TORR	0.5 MIN	77	112	131	73	98	126
	10 MIN	70	120	123	52	82	77
BULK TUNGSTEN		56	60	70	56	60	70

*Full Width at Half Maximum

intensities) for only those three basic orientations presented in the tables (Also see Appendix F).

Peak width values, measured at full width at half maximum (FWHM), for each diffraction peak are given in Table 7. Bulk tungsten FWHM values were measured from a 0.25-mm thick, 99.98%-pure AESAR tungsten foil. As a result of the nature of x-ray diffraction, increasing diffraction angles give increasing FWHM values. Therefore, FWHM values for only the peaks at the same diffraction angles (i.e., the same orientations) are used to make a comparison among the samples. Better crystal quality and/or thicker film are known to decrease FWHM [31]. Table 7 shows that FWHM decreases with increasing deposition temperatures and longer deposition times (thicker films). The only exception to the latter is FWHM for α -W(200) at 1 torr-285°C. Higher temperatures are expected to enhance crystallization. Longer deposition times allow crystals to grow larger. Both factors help the crystals approach an ideal case where the peak broadening, or FWHM, is minimum.

Film Resistivity

Deposited tungsten film resistivities were calculated from sheet resistance values (Equation 8). Figure 48 presents resistivity versus thickness for 4-minute reaction times (sample mounted in horizontal position). Film thickness values

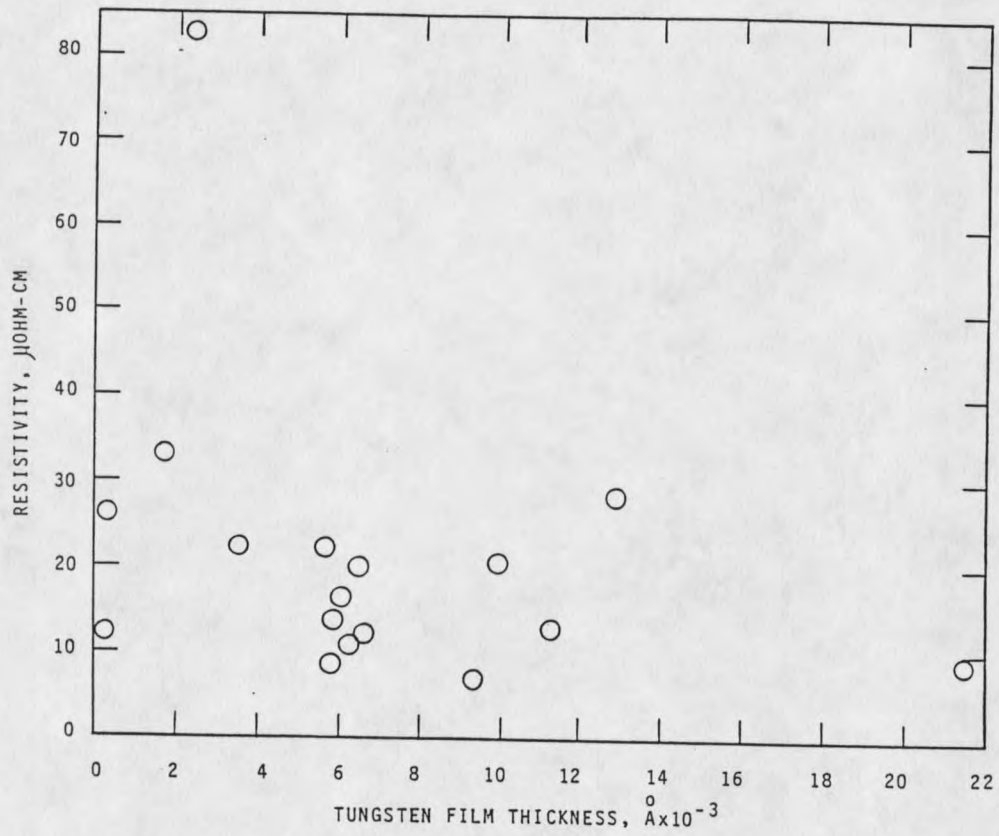


Figure 48. Resistivity versus W film thickness. ($t = 4$ min, sample horizontal)

used were those calculated from the gravimetric, constant-density analysis, for which a constant film density (19.3 g/cm^3) was assumed. Reported values for resistivities (and sheet resistances) correspond to the measurements performed at the center of the tungsten-deposited Si wafers. Figure 48 includes all deposition conditions for the temperature and pressure range examined. The resistivities were found to be higher than tungsten bulk resistivity, $5.6 \mu\Omega\text{-cm}$ at 20°C .

The changes in sheet resistance with deposition time for 10 torr and 1 torr reaction pressures are presented in Figures 49 and 50, respectively. The films deposited in less than 2-minute reaction times are still in the island/coalescence stage as evidenced by SEM pictures. These film resistivities cannot be approximated by the tungsten bulk density, because they are more porous than a conventional continuous film. Thus, the thickness found by using bulk density cannot be employed in resistivity calculations. For resistivity, the actual film thickness found by SEM, stylus profilometer, or a similar method is needed. Therefore, the abscissa and ordinate of Figure 49 and 50 are sheet resistance and inverse time rather than resistivity and thickness. Since film resistivity is the product of sheet resistance and thickness (Equation 8), higher slopes in the figure imply higher resistivities. The highest slope is found in Figure 49 for the 10-torr, 295°C -deposition condition while the other conditions have slopes rather close to each other. The values for longer reaction

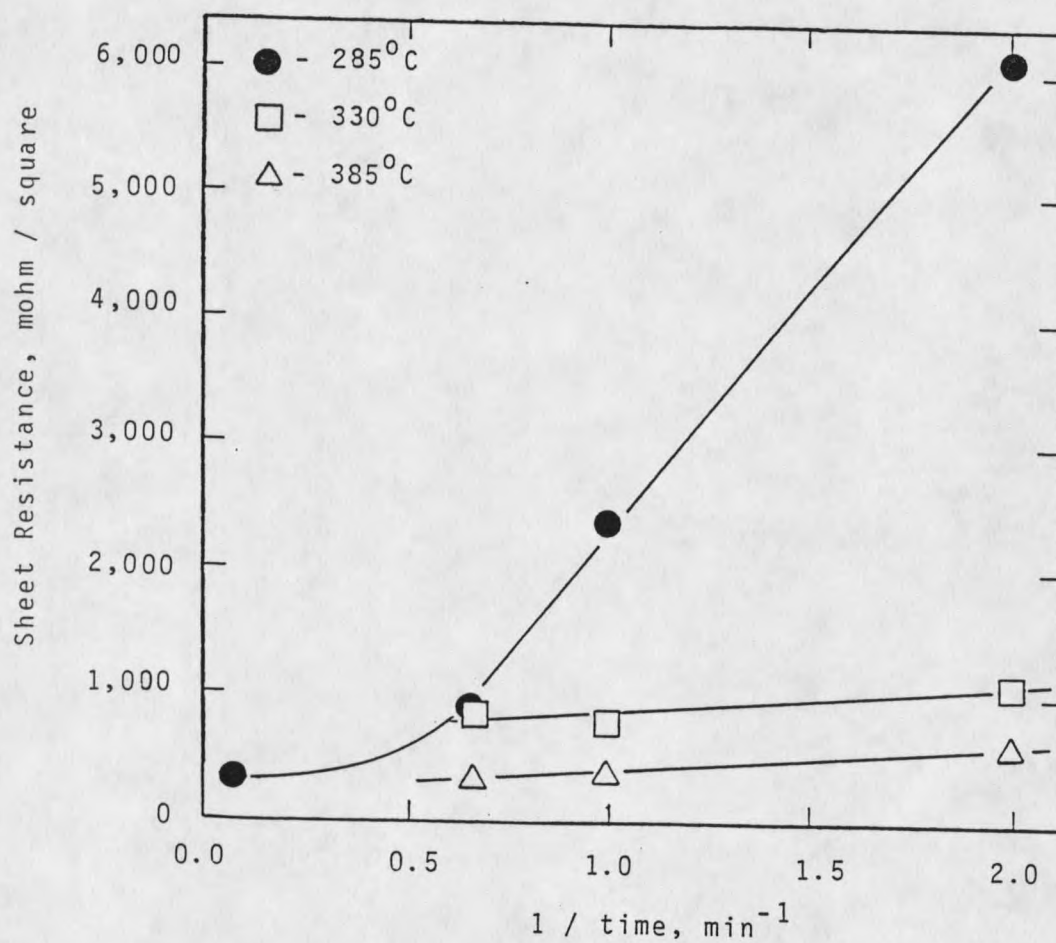


Figure 49. Sheet resistance versus inverse deposition time for $P = 10$ torr (vertical substrate).

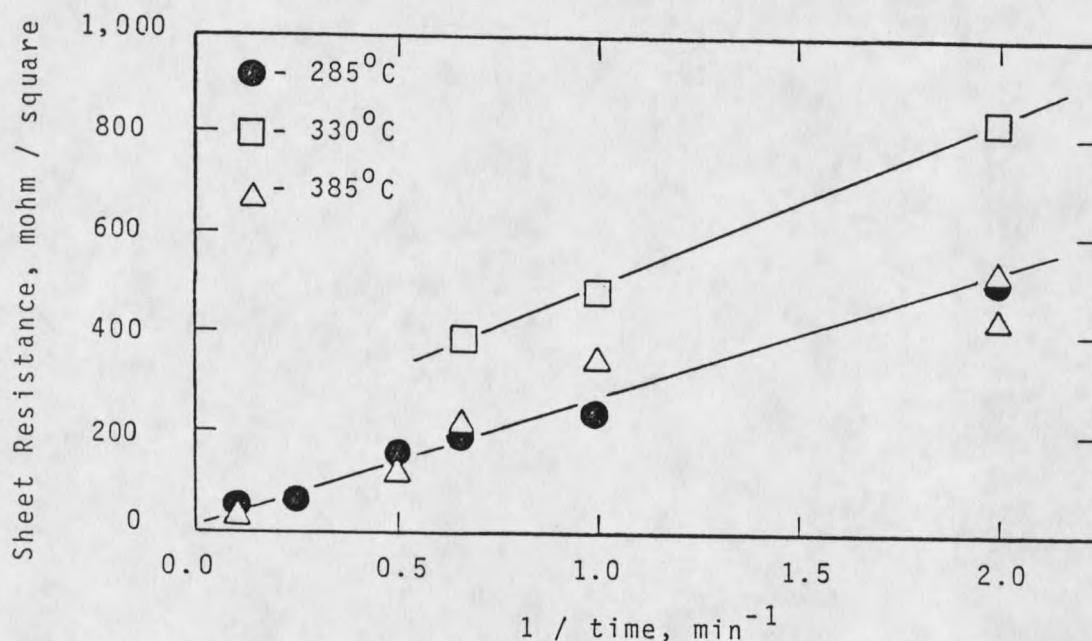


Figure 50. Sheet resistance versus inverse deposition time for $P = 1$ torr (vertical substrate).

times (10-12 minutes), where continuous films form, are also shown in the figures. In a conventional plot of sheet resistance versus inverse thickness, a straight line implies that the film resistivity and thereby the film structure is constant. A considerable change in slope occurs for 10 torr-285°C when deposition time increases from 1.5 minutes to 12 minutes, indicating a change in resistivity probably because of a change in the film structure.

DISCUSSION

The experimental results are interpreted in three main sections:

- (i) Verification of Kinetic Tungsten Deposition: The rationale is presented that the reaction is kinetically controlled, the film is tungsten without silicide formation and without significant impurities, and mass transfer does not affect the results.
- (ii) Kinetics and Morphology: The tungsten crystal structures obtained as the films grow are shown to be related to the kinetic steps.
- (iii) Film Properties: Dependence of some important film properties on reactor conditions is discussed.

Verification of Kinetic W Deposition

Impurity Content

Possible atomic impurities in the W films include oxygen (O), carbon (C), silicon (Si), and fluorine (F). The presence of Si and F are reported to increase film resistivity for the W films deposited by the $\text{SiH}_4\text{-WF}_6$ reaction [120,122].

Oxygen is present on the silicon substrate surface in the form of a native oxide layer. Even after the treatment with

dilute HF solution, there is evidence for the presence of surface oxygen on Si wafers [111]. Tungsten formed by the Si reduction of WF_6 can result in oxygen concentrations as high as 25%, whereas the H_2 reduction yields W films with less than 1% oxygen [85]. It is believed that H_2 acts as an O_2 getter to form H_2O . Then, considering the nature of reactants, one can expect SiH_4 to getter oxygen also since it is more reactive with oxygen (pyrophoric, $\Delta G^0 = -298$ kcal/mole) than is H_2 (flammable, $\Delta G^0 = -58$ kcal/mole). Accordingly, Sivaram, et al. [126] reported a similar level of oxygen in H_2 - and SiH_4 -reduced films. AES depth profiles presented in Figures 30, 31, and 32 show an "unchanging" oxygen concentration of about 5 to 9% throughout the W films. Oxygen can be incorporated into the films after deposition upon exposure of the W deposit to air. High film porosity enhances the oxygen incorporation. Incorporation of oxygen in the films from the native oxide layer would lead to a peak at the W-Si interface in the AES depth profiling. It is noted that there is no oxygen concentration peak at the Si-W interface, showing that the native oxide has been displaced by HF treatment and/or oxygen-gettering action of SiH_4 . The higher oxygen contents observed in the present AES depth profiling (5-9%) than the 1% observed by Sivaram, et al. [126] most probably results from the exposure of the films to air before analysis.

Exposure to air is also believed to be the reason for the presence of carbon (C) in the AES spectra. Carbon has not been

reported as a significant impurity in a clean deposition environment.

As stated in the results section, silicon (Si) content in the films was below the noise level for the AES system used in these analyses. Low Si concentrations rule out any major silicide formation reaction (mainly WSi_2 and W_5Si_3 , see Table 1). It is known that high SiH_4/WF_6 ratios (higher than ~ 1.3) yield high Si concentrations in the W films [104,118,120,121]. The stoichiometric ratio of reactants for the silane reduction system is $\text{SiH}_4/\text{WF}_6 = 1.5$ (Table 1). When the reactant ratio is $\text{SiH}_4/\text{WF}_6 = 1.0$, which is the case in this study, SiH_4 is the limiting reactant. Thus, all the Si coming from SiH_4 decomposition is expected to react with WF_6 to form W and SiF_4 . However, this depends on the relative sticking coefficients of WF_6 and SiH_4 on the Si substrate and W surfaces and assumes that the adatoms (or adsorbed groups) are able to diffuse, meet, and react on the surface.

High Si concentration (19%) is observed only for the W film formed at the 10 torr-137°C deposition condition (Figure 30). It has been reported that Si concentration in W films increases with decreasing deposition temperatures [120,121]. However, the more probable explanation for this high Si content is related to the influence of the very small average film thickness of 300 Å. As mentioned in the results section, the AES analysis performed at different surface locations on this film before the depth profiling showed some non-

uniformity in W concentration. This implies different film thicknesses across the surface where thin-film nucleation towers (islands) exist. Thus, for the regions where the W thickness is less than Auger electron escape depth, which is less than 50 Å, electrons coming from the Si substrate can easily contribute to the Si signal. In addition, non-uniform thickness may leave some areas of the surface without any W covering.

The fluorine (F) content in all films is below the detectability limit for Auger analysis. CVD tungsten films are generally known to be high in F content due to the incorporation of fluorine-rich reactant and product gases in the growing films [122,126] (namely, reactant gas WF_6 , product gas HF in H_2 reduction, and SiF_4 in SiH_4 reduction). Sivaram, et al. [126], using SIMS analysis, observed an F/W ratio changing between 0.04 and 0.2 for the SiH_4 - WF_6 reaction system when the reaction is carried out between 300 and 550°C. In this study, AES was the only technique used to monitor F concentration. Other tools, such as secondary ion mass spectroscopy (SIMS) and neutron activation analysis (NAA) are required for a better understanding of F content in the tungsten films.

In summary, AES analysis implies that only the tungsten formation reaction takes place under the experimental reaction conditions and that except for oxygen the impurity level in the air-exposed films is very low.

Kinetic Region Gas Flow Rate

Reactant flow rates were carefully chosen to insure that the reaction was kinetically controlled. The reactant gas flow rate was kept constant for each set of constant-pressure-deposition tests in order to acquire rate data dependent only on temperature. The highest attainable reactant flow rates, $WF_6 = SiH_4 = 120$ sccm for 10 torr and $WF_6 = SiH_4 = 110$ sccm for 1 torr, were used for the deposition experiments. These values are about one order of magnitude larger than those used in commercial CVD reactors. The flow rates chosen for the experiments are in the plateau region where the deposition rate does not change with gas flow rate (Figure 29). Such a choice corresponds to region III in Figure 16 and meets the requirement for kinetic studies. A differential reactor requires less than 10% conversion of reactants. Calculations performed to find the fractional conversion of reactants show that far less than 10% of the reactant gases react on the substrate surface (Appendix B). Condensation of the reactants on the reactor wall, when included in the calculations, increases this percent conversion for the system as a whole. The amount of condensation is not known, but Figure 29 suggests that for flow rates higher than ~60 sccm WF_6 or SiH_4 condensation is not significant. The sporadic behavior of the data observed in Figure 29 may be because

- (a) the flow patterns change in the reactor with gas flow rate,

- (b) there is a change in the order reactants are introduced into the reaction chamber, or
- (c) there are differences in substrate surface conditions.

Gas flow Reynolds numbers through the system were very small, as shown in Appendix D, suggesting a laminar flow regime. Another evidence for laminar flow is the pattern of dark deposits observed on the reactor walls. When WF_6 gas is adsorbed on the reactor wall, it forms tungsten oxides and oxyfluorides upon exposure to air, yielding a residue which is dark blue in color. Patterns observed appeared to be "negative shadows" from the protrusions on the inside wall of the reactor. These "negative shadows" circumscribed a very clean reactor wall surface while the other parts of the reactor walls were covered with the dark deposit. The undisturbed lines of negative shadows observed in the direction of flow imply the presence of a region free of WF_6 exposure which is a result of a laminar flow regime. Hence, one can expect a different intensity of mixing for reactant gases at different gas flow rates. This creates different reactant ratios on the substrate surface, yielding different reaction rates. Nevertheless, this is not a factor in the present kinetic studies since the consistency in the experiments is maintained by employing one set of flow rates only ($WF_6 = SiH_4 = 110$ sccm, $Ar = 64$ sccm). The flow rates for the 10-torr experiments, WF_6

= SiH_4 = 120 sccm, Ar = 70 sccm, with the horizontal Si substrate positions are the only exception to this.

At the beginning of each experiment, the system pressure and temperature is stabilized with the Ar flow, then the reactant gases, WF_6 and SiH_4 , are introduced into the chamber simultaneously. Manual control of the valves for reactant gases is necessary in the present reactor system to prevent leakage through the mass flow controllers which are attacked by the corrosive nature of the WF_6 gas. Therefore, the order in which reactant gases are introduced into the chamber is dependent on operator skill and may be expected to change in each run. This results in different nucleation densities on the fresh Si substrate surface which in turn affects the growth rate.

The predicted effect of the native oxide layer and surface roughness on the growth phenomena is discussed in the Impurity Content section and in Chapter 2. Thus, different surface conditions for the silicon substrate can give different growth rates at the same gas flow rate, contributing to the sporadic behavior in Figure 29.

Effect of Substrate Position on Kinetics

Tungsten deposition rates for horizontal and vertical substrate positions are given in Figure 33 and 34, respectively. Average rates for the vertical position are higher than those for the horizontal position. Film uniformity was deduced from the sheet resistance measurements performed on different locations across the W-deposited substrate surface. Excellent thickness uniformities are observed for tungsten films deposited with a vertical substrate position, whereas remarkable changes in the film thickness at different positions on the wafer are recorded for those films deposited with a horizontal position. Under normal circumstances, this is explained by a mass transport controlled process (see Chapter 2) [49]. However, the absence of mass transport limitations is proven later in the Proposed Kinetic Steps section. Condensation of the reactant gases and the reactor geometry are decisive factors in thickness uniformity since they can change the reactant composition across the substrate surface. The average distance traversed in order for the reactants to reach the substrate surface is longer for the horizontal substrate position than that for the vertical position. Therefore, in the horizontal case, reactants are subjected to collisions with more reactor wall area. This leads to more condensation. Different levels of condensation for WF_6 and SiH_4 on the reactor wall can cause a different reactant ratio on the substrate surface. Thus, gas phase stoichiometries on the

substrate surface are probably different for the horizontal and vertical cases. The presence of laminar flow, in which mixing of reactants is limited, exacerbates the situation for the horizontal position.

Kinetics and Morphology

Morphology, Nucleation and Growth

SEM micrographs for tungsten surfaces indicate that the morphology of the tungsten film is strongly influenced by deposition conditions. Lower temperatures and higher pressures produce porous films, while higher temperatures and lower pressures result in continuous films with smoother surfaces. This finding is in agreement with Ohba, et al. [119].

It is known that 2-dimensional growth produces continuous films with minimum porosity. This kind of growth requires that adatoms have enough surface mobility to migrate to proper ledge-kink sites on the growing crystal where they are incorporated into the growing crystal [53]. When the surface mobility is inhibited or when the condensation rate is relatively faster than the surface migration rate, atomic rearrangement on the growing surface remains incomplete. In such a case, growth is more dependent on gas phase impingement than surface migration. This sort of growth produces porous structures (3-D growth) and extensive lattice defects.

The change in W film crystallinity with deposition temperature can be observed in Figures 36 and 37. Higher deposition temperatures produce crystal aggregates which are sharper in shape as shown in Figure 36. This indicates a better crystal quality. Since surface diffusion is an activated process, higher temperatures provide more energy for adatoms to migrate and produce well-defined crystals [53].

Plan-view and cross-sectional micrographs (Figure 41-44) show the effect of temperature on the formation of thick films. At 10 torr, a less porous film with more crystalline-shaped aggregates is obtained at the higher temperatures. At 1 torr, a continuous film with a columnar structure throughout the whole thickness is obtained at 385°C, whereas at 285°C there is porosity at the W-Si interface. In the latter case there appears to be an interface effect related to initial nucleation of tungsten on the Si surface. Figure 44 also shows that although a porous structure is present at the interface, some aggregates grow faster at the expense of others to produce a final continuous structure for the thick film.

It has been reported that the substrate surface plays an important role in determining film morphology [118,119]. The amount of the native oxide layer on the silicon surface changes the film structure [111]. Smoother films can be obtained when removal of the surface oxide layer is more complete with a technique such as NF_3 plasma treatment in addition to standard HF dip. It has been also reported that

WF_6 is capable of etching this native oxide layer [6,111]. The etching rate is higher and more uniform at higher temperatures. Thus, higher temperatures provide a more uniformly etch-prepared Si surface for the initial W nucleation stage which yields smoother Si-W interfaces.

Based on the above, better film morphologies at higher temperatures may be attributed to

- (1) higher adatom surface mobility.
- (2) more complete removal of the native oxide layer by WF_6 etching.

SEM micrographs of W films deposited at 10 torr, 330 and 385°C for 0.5 min reaction times shown in Figures 35, 55 and 56 indicate an initial tungsten layer formation with a structure comprised of 2-D islands. This initial layer is not seen clearly for the 285°C deposition temperature (Figure 54), probably because of the limitations in obtaining a good contrast for those SEM micrographs. Upon this initial quasi-2-D layer, secondary tungsten nucleation and growth seem to occur. Therefore, tungsten aggregates growing 3-dimensionally are a result of W nucleation on an initially formed tungsten layer. Such a growth mode resembles the Stranski-Krastanov mode in which 3-D crystals grow on top of one or a few initial monolayers of the deposit. This implies that the W film and the Si substrate are very similar in terms of surface free energies (i.e. $\sigma_w \approx \sigma_{\text{Si}}$, $\sigma_{\text{W/Si}} \approx 0$). However, this condition can be fulfilled for only a few monolayers. Then, $\sigma_{\text{W/Si}}$ goes

through a change with the size and shape of the island as the film grows. Hence, a transition between the two modes (Transition from 2-D to 3-D) occurs when Λ becomes positive (Equation 3). Three-dimensional crystallite formation tends to expose as much bare substrate area as possible to minimize the surface free energy of the system (In this case, the substrate is the quasi-2-D tungsten layer).

In order to achieve an analysis of the initial nucleation density, each nucleus should be distinguishable (i.e. before coalescence starts). SEM micrographs show that a 0.5-min reaction time is too long for nucleation analysis, even for the secondary tungsten nucleation (i.e. tungsten on tungsten). For a dependable analysis of the initial nucleation rate, experiments need to be performed for much shorter reaction times (<0.5 min), where initial nuclei are still distinct and countable. In the present reactor system, however, the attainment of accurate reaction times shorter than 0.5 min is not possible because of the limitations in the pumping speed and mass flow controllers. Upon the introduction of reactant gases in addition to Ar flow, it takes 15-20 seconds in order for the pressure to stabilize. Therefore, the data for 0.5-min reaction times are not representative of a steady-state operation. A semiquantitative analysis of tungsten nucleation density with respect to deposition temperature gives quite sporadic data for 0.5 to 1.0-min reaction times. This can be attributed to an unsteady-state operation.

SEM micrographs for 1.5-min reaction times for both 10 torr and 1 torr (Figures 36 and 37) show that the number of aggregates increases with increasing deposition temperatures. This is an indication of higher nucleation rates at higher temperatures. Such a behavior can be explained with initially incomplete condensation as discussed in Chapter 2 (Figure 1). At higher temperatures, adatoms have more tendency to re-evaporate before joining larger clusters. This decreases the size of capture zones, creating more surface area available for further nucleation. Another explanation for the higher nucleation densities at higher temperatures can be activated adsorption. At low temperatures, nucleation occurs at sites which are energetically the most favorable. Higher temperatures can induce changes on the surface and create more active sites for nucleation [127].

Aggregate size achieved under 10 torr reaction pressure increases with increasing deposition temperature (Figure 36), whereas for 1 torr it is almost insensitive to temperature (Figure 37). The average size for 1 torr-385°C appears less than that for 285 and 330°C. Also, note that porosity is already lost at 1.5 min under this 1 torr-385°C condition. When the aggregates touch each other, their growth essentially stops. Sometimes the voids among the larger aggregates are filled with other aggregates growing on a lower plane. As a result, average size appears to be smaller. Average aggregate size at 1 torr is larger than that at 10 torr when deposition

time and temperature are comparable. Then, for shorter reaction times, it can be stated that aggregate size is a direct result of deposition rate.

As a compendium, tungsten film morphological studies here suggest the following:

- (1) Surface mobility of adatoms is higher at higher temperatures and lower pressures.
- (2) Nucleation rate of tungsten on tungsten is higher at higher temperatures.
- (3) For shorter reaction times, while the films are porous, aggregate lateral growth rate is directly related to deposition rate.

Crystal Structure

The change in crystal orientation of tungsten films with thickness and deposition conditions is given in Table 6. Crystal structure of tungsten films involves two different deposition mechanisms [128]: an initial growth of tungsten on the Si surface, followed by the growth of tungsten on this initial layer. The former involves adsorbate-substrate interactions and lattice match between the substrate and the growing film which determines the level of interface epitaxy. The latter mechanism is an inherent feature of growth of the film, and the preferred crystal structures and adatom mobility on these surfaces may lead to self-epitaxy. However, self-epitaxy is strongly dependent on interface epitaxy. These

mechanisms will be discussed separately in the following paragraphs. The discussion of crystal structure is in reference to the epitaxial growth mechanism, even though determining epitaxial film growth is not an objective of the experiments. In this way, it is easier to understand the change in crystal orientation and deposition mechanism with experimental deposition conditions.

Tungsten Growth on Si: Tungsten and silicon have quite different lattice parameters in addition to different crystal structures. Table 8 summarizes the lattice mismatch between Si(100) substrate and W crystal surfaces and compares the interatomic distances for the observed major tungsten film orientations, namely W(100)* and W(110). High values for lattice mismatch ($\epsilon > \pm 15\%$) would indicate a great difficulty for obtaining an epitaxial growth of W(100) orientation on a Si(100) surface. Mismatch in lattice parameters is generally mitigated by the formation of a coincidence lattice [129]. Adsorbate-substrate and adsorbate-adsorbate interactions play an important role during the formation of the coincidence lattice.

* W(200) and W(100) surfaces are identical surfaces in a bcc structure. The results given in Chapter 4 in terms of a W(200) orientation are direct interpretations from Reference [33]. In the literature, W(100) nomenclature is more commonly used and it is employed here throughout the discussion.

Table 8. Lattice Mismatch, ϵ , Between Si and W Crystal Surfaces..

Crystal	Crystal structure	Lattice constant, Å	Crystal orientation	In-plane lattice geometry	In-plane interatomic distance, Å	$\epsilon = \frac{b-a}{a} \times 100, \%$
Si	fcc	5.43	(100)	square	$a = 3.84$	0.0
W	bcc	3.16	(100)	square	$b = 3.16$	-17.7
			(110)	diamond	$b_1 = 3.16$ $b_2 = 2.23$	-17.7 -41.9

It was observed that the phases formed by depositing metals onto Si depends strongly on the amount of metal deposited. In the case of deposition and annealing of Ni on Si(111) surfaces, two types of epitaxial NiSi_2 orientation were observed [130]. Upon annealing of a 10-Å Ni film on Si(111) surface at 450°C, type-B orientation (where the lattice is aligned with the Si lattice) was observed, whereas 20-Å deposits resulted in type-A orientation (where the lattice is rotated 180° with respect to Si lattice). A metastable intermediate phase, $\theta\text{-Ni}_2\text{Si}$, grew at 300°C as a precursor phase of type-A NiSi_2 . Similarly, (110) oriented CoSi_2 deposition on Si(100) surfaces using a template technique exhibited two epitaxial orientations [131]. The physical mechanism which leads to different orientations is not well understood yet but is ascribed to the morphology of the initial Si(100) surface.

In the case of CVD of W on Si(100) wafers by the $\text{SiH}_4\text{-WF}_6$ reaction, Itoh, et al. [110] observed a $\beta\text{-W}$ formation along with $\alpha\text{-W}$ for very short reaction times (~15 s). For longer reaction times (~90 s), x-ray diffraction showed only $\alpha\text{-W}$ peaks. In the present research, reaction times shorter than 30 seconds were not used since the objective was the study of kinetics. It is the author's interpretation that a metastable $\beta\text{-W}$ formation observed by Itoh, et al. [110] occurs at the interface to moderate the lattice mismatch between Si(100) and

α -W surfaces. Such an interpretation is in analogy with θ - NiSi_2 formation in Ni deposition on Si(111) [130].

Chang [128] has stated that the initiation of a bcc(100) growth on an fcc(100) lattice is a real challenge. The bcc metals, when grown on an fcc(100) surface, prefer (110) orientation due to lack of bonds among neighboring atoms. In this study, W(110) orientation is prevalent at the Si-W interface as evidenced by x-ray diffraction analysis (see Table 6 for shorter reaction times). High lattice mismatch, ϵ , values presented in Table 8 suggest a great deal of rotation between W(110) and Si(100) lattice.

Tungsten Growth on W: Adatoms need to migrate on the surface and meet each other to form final reaction products. If surface adsorption and diffusion controls the mechanistic steps, as will be discussed in more detail, then a high surface diffusion rate is a required condition for high reaction rates. It is known that surface diffusion rate is orientation dependent as mentioned in Chapter 2. Thus, surfaces with different orientations give different deposition rates if surface diffusion is an important kinetic factor. In Table 6, the change in crystal orientation with deposition temperature and pressure is clearly seen. Thus, the deposition rate may well change with the W crystal orientation (see Table 6 and Figures 33 and 34). The observed increase in W(100) orientation with thickness (except at the 10 torr-285°C

condition) is similar to that reported by Kamins, et al. for the H_2 reduction reaction [96]. In order to understand the change in orientation from W(110) to W(100) with thickness and deposition conditions, it is important to know the characteristics of these surfaces. The (110) plane of bcc is atomically smooth, making surface diffusion easier, while the (100) plane is more open and substrate potential periodicity (i.e. periodicity of potential wells across the surface) produces barriers to surface diffusion and indicates a higher activation energy for surface diffusion. Among the many examples of metal deposition on single crystal metal surfaces, the pertinent ones are the growth of Cu [132], Pd [133], Pb [134], and Be [135] on W(110) surface; and Cu [132], Ag [136], and Pd [137] on W(100) surface. All layers were observed to grow in the SK mode with 1-3 monolayers before 3-D crystals formed. Because of the low activation energies provided, many of the 3-D crystals form on the (110) surfaces at 300K.

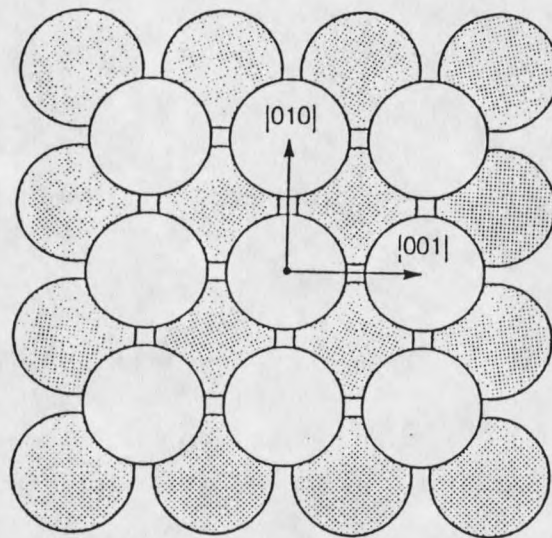
Epitaxial growth studies on bcc(100) surfaces showed a random orientation at low temperatures [138]. In the submonolayer range, order was seen only upon heating to 600-800 K. Order was not observed at low temperatures because of the atomic roughness on the surface. The adatoms prefer to seat deeply in the potential troughs of the surface yielding a random distribution of the film atoms. Order obtained at high temperatures was attributed to the inherent instability of the bcc(100) surface. At high temperatures, reconstruction

of the surface may easily occur and alter the previous geometric considerations. As a result, rapid surface diffusion is obtained on a reconstructed bcc(100) surface and a higher reaction rate is possible and expected, and an apparent very low activation energy is present. A schematic diagram of a W(100) surface before and after the reconstruction is shown in Figure 51 [139]. After the reconstruction, a zig-zag displacement of top layer W atoms takes place and the periodicity is (2x2).

Based on the above discussion, the higher percent intensity of W(110) orientation at lower temperatures can be explained by the lower activation energy for surface diffusion on bcc(110) surfaces. Then, the increase in W(100) intensity at higher temperatures is because of the reconstruction of bcc(100) surfaces in such a way that surface diffusion is easier on the resultant surface. Hence, at higher temperatures (100) orientation dominates as the film thickness increases (higher deposition times). At 1 torr, this leads to a self-epitaxial growth.

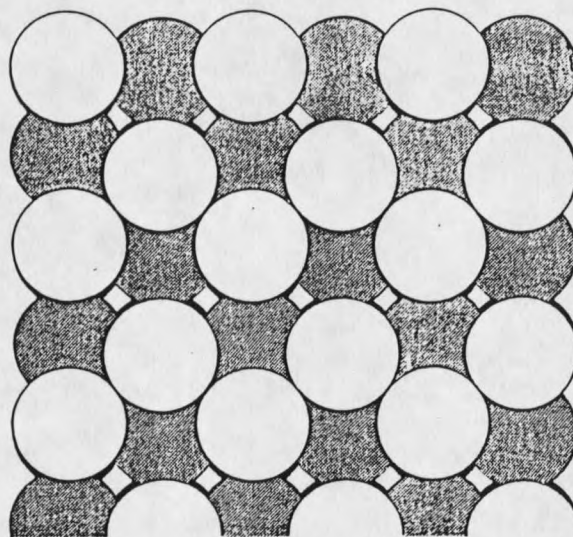
The dependence of the W crystal orientation on reaction pressure (Table 6) can be explained in terms of adsorbate-substrate interactions. Densely packed surfaces such as bcc(110), fcc(111) and hcp(0001) surfaces are known to have limited interaction with adsorbate molecules. Thus, adsorbate-adsorbate interactions are much stronger on these surfaces than are adsorbate-substrate interactions. Rhodium adsorbed on

(a)



bcc (100)

(b)



W (100) - c (2 x 2)

Figure 51. Schematic diagrams of W(100) surfaces (a) before reconstruction, (b) after reconstruction [139].

a W(110) surface is a good example for this case [140]. One can expect that a change in pressure, thereby a change in adsorbate surface coverage, does not significantly alter the W(110) surface characteristics.

It was indicated earlier that at high temperatures surface reconstruction occurs on W(100) surfaces. This reconstruction increases the adsorbate surface diffusion rate which in turn enhances W(100) growth at the expense of other orientations. Table 6 shows that the enhancement in W(100) growth is remarkably higher at lower pressures when the temperature is kept constant. This observation may be an indication that adsorbate-substrate interactions at high adsorbate coverages (at high pressures) hinder the reconstruction process on W(100) surfaces. This subject should be clarified by performing surface science studies on single crystal W(100) surfaces with different coverages of SiH_4 and WF_6 gases as adsorbate molecules. Then, it can be determined which molecule is more influential in surface reconstruction.

Crystallinity and Crystal Size: X-ray diffraction peak widths of deposited tungsten films and of bulk tungsten foil are given in Table 7. The values for bulk tungsten provide a basis for determining how much the W films approach the bulk values in terms of crystal size and crystallinity. It should be kept in mind that crystal structure in the commercial tungsten foil is affected by the manufacturing process. Table

7 shows that at longer reaction times and higher temperatures the crystals had FWHM values close to those for bulk tungsten foil. Higher deposition temperatures produced crystals with smaller FWHM values at both 1 and 10 torr. This could be due to (a) better crystal quality, or (b) larger crystal sizes as a result of higher growth rates [31]. Better crystal quality is the preferred explanation, since adatoms at higher temperatures have higher energies to migrate to proper lattice sites. SEM pictures do not provide much evidence for larger crystal formation at higher temperatures. For example, the tungsten aggregate size at 1 torr is almost insensitive to temperature (Figures 38-39, 41-42). The grain sizes estimated from the Scherrer formula are given in Table 9 (see Appendix G for the use of Scherrer formula) using the α -W(110) peak width for grain size calculations. Calculated grain size values are the same order of magnitude as those reported by M. Suzuki, et al. [120] for the $\text{SiH}_4\text{-WF}_6$ system. Table 9 shows that calculated grain sizes are about one order of magnitude smaller than aggregate sizes measured from the SEM micrographs. This suggests that each aggregate is composed of polycrystals or has a mosaic structure containing single microcrystals [31]. An exaggerated diagram for a possible mosaic structure is presented in Figure 52. Indeed, for 1 torr-285°C (Figure 42) very small distinct tungsten nuclei on the continuous tungsten film are clearly seen. A crystal aggregate with mosaic structure does not have its atoms

Table 9. Calculated Grain Sizes* and Measured Aggregate Sizes** For Tungsten Films.

		285°C		385°C	
		Grain Size, Å	Aggregate Size, Å	Grain Size, Å	Aggregate Size, Å
10 TORR	1.5 MIN	140	1,600	220	4,080
	12 MIN	260	3,950	280	2,730
1 TORR	0.5 MIN	190	2,630	200	3,180
	10 MIN	210	15,200	290	3,830

* Calculated from FWHM values for α -W(110) peaks using Scherrer formula

** Measured from SEM plan-view micrographs

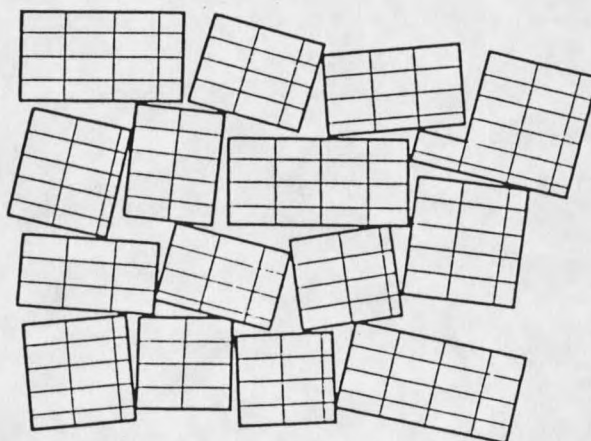


Figure 52. The mosaic structure of a real crystal [31].

arranged on a perfectly regular lattice extending from one side of the crystal aggregate to the other. Instead, the lattice is broken up into tiny blocks, each slightly disoriented one from another.

Initial crystal size is basically determined by the number of nucleation sites on the silicon substrate and corresponding size of the capture zones. The difference in lattice parameters of Si and W is also an important factor in the formation of the initial crystal structure.

Longer reaction times at each deposition condition give crystals with smaller FWHM values (Table 7). W(100) orientation for 1 torr-285°C exhibits an increasing FWHM for longer reaction times. The reason may be that there are higher

nucleation densities of tungsten on W(100) surface than on Si(100) surface at this deposition condition. In this circumstance, crystal size decreases and gives a higher FWHM.

Lower pressures for longer deposition times (W growth on W) give larger FWHM values at 285°C (Table 7). The deposition rate at 1 torr is higher than that at 10 torr. It appears that at low pressures microcrystal size decreases. This may be due to more nucleation of tungsten on W surfaces at lower pressures which results in smaller microcrystal sizes. Such a case may be true if there is a competitive adsorption; at lower pressures competitive adsorption would be less severe, yielding more adsorption sites (and in turn more nucleation sites) for the less strongly adsorbed reactant. At 385°C and longer deposition times, FWHM values are almost the same (except for W(100) orientation). This can be explained by the surface characteristics of bcc(100) orientation. Reconstruction of the bcc(100) surface may provide more nucleation sites through adsorbate-substrate interactions, and it is possible that this reconstruction is hindered at high pressures to give less nucleation sites.

Proposed Kinetic Steps

Complicated behavior in Arrhenius plots observed by previous researchers is discussed in Chapter 2. It is the author's opinion that there are two main reasons that previous researchers were unable to obtain the activation energy:

- (1) Differential reactor conditions were not provided causing the reaction surface to be starved for reactants.
- (2) Thickness for W films was found by measuring apparent physical thickness, which is dependent on film morphology, rather than measuring the amount of W deposited (i.e. moles or grams of W formed).

In this research, high reaction gas flow rates and the gravimetric method used for the Arrhenius activation analysis have overcome the limitations of previous research.

Arrhenius plots given in Figures 33 and 34 show the complexity of the $\text{SiH}_4\text{-WF}_6$ reaction system. The change in apparent activation energy with deposition pressure implies a change in the controlling mechanism for the reaction. An activation energy of 0.35-0.40 eV/atom for 10 torr is a typical range for surface-activated processes. All the allowable reaction pathways in tungsten deposition with the $\text{SiH}_4\text{-WF}_6$ reaction system have been reported to be exothermic [105]. Dependence of the apparent activation energy on the heat of reaction is discussed in Chapter 2. High apparent activation energy for 10 torr strongly supports a surface kinetically controlled regime since the process is exothermic [52].

For 1 torr, deposition rate is less sensitive to reaction temperature giving an activation energy of 0.08-0.12 eV/atom. There may be two reasons for such low activation energies:

- (1) There are insufficient amounts of reactants reaching the substrate surface because of diffusion limitations or very low reactant gas flow rates.
- (2) Adsorption/desorption phenomena are the controlling mechanism as a single elementary surface process.

The high reactant flow rates chosen in this study rule out the possibility of gas flow limitations (as discussed previously). Diffusion does not seem to be a controlling mechanism either, as will be shown. It is known that the gas phase diffusion rate increases as the pressure is lowered. With decreasing pressure, the diffusion rate can finally become so fast that the heterogenous chemical reaction becomes the slowest step [62,141]. The mass transport effect then becomes smaller at lower pressures than one calculates, assuming diffusion to be rate determining. Strong temperature dependence of the rate for 10 torr indicates that there is no mass-transport-related limitation at this pressure. Therefore, one can expect no mass-transport-related limitation at 1 torr either. Gas phase nucleation of tungsten, which may deprive the substrate surface of the reactants, is another factor to be examined [142]. In the case of high gas phase nucleation rates, the Arrhenius plot would exhibit mass transfer limitations where rate is insensitive to temperature. Higher gas phase concentrations (higher reactor pressures) yield higher gas phase nucleation rates. However, temperature dependence of the reaction rate for 10 torr reaction pressure

is stronger than that for 1 torr pressure (Figures 33 and 34). Observed temperature dependencies of the rates at higher pressures refute the presence of rate limitations due to possible gas phase nucleation of tungsten. Therefore, insufficient supply of the reactants to the surface cannot be the reason for the temperature insensitive behavior for 1 torr reaction pressure. Table 10 compares the experimental W deposition rates with theoretical ones when it is assumed that all the SiH_4 reaching the substrate surface reacts (See Appendix E for calculations).

An explanation of low activation energy for 1 torr based on adsorption/desorption phenomena is more plausible. SEM analyses reveal that nucleation rate (tungsten on W) increases with decreasing temperature for both 1 torr and 10 torr. This corresponds to an initially incomplete condensation, as explained in Chapter 2, which occurs at high temperatures or low impingement rates (low pressures) [22]. Initially incomplete condensation is more pronounced at lower pressures, as the impingement rate is less. At higher temperatures, adatom re-evaporation is higher which results in smaller reactant mean-residence time on the surface. Adsorption rate, however, does also increase with increasing temperature. Temperature and pressure dependence of adsorption and desorption are given in Chapter 2 [17]; the rate equations are:

Table 10. Tungsten Deposition Rates at 285°C, Experimental versus Theoretical at $X_{\text{SiH}_4} = 1.0$.

DEPOSITION PRESSURE	TUNGSTEN DEPOSITION RATE, Å/MIN	
	Theoretical ($X_{\text{SiH}_4}=1.0$)	Experimental
1 torr	7,200	4,000
10 torr	7,900	1,000

Rate of adsorption,

$$\mu_a = \frac{P}{\sqrt{2\pi mkT}} \sum_{i=1}^m n_i \sigma_i f(\theta_i) e^{-E_i/RT} \quad (27)$$

and rate of desorption,

$$\mu_d = \sum_{i=1}^m n_i K_i f'(\theta_i) e^{-E_i'/RT} \quad (28)$$

Rate of both adsorption and desorption increase with increasing temperature due to the exponential terms. However, Equation 27 has an extra $T^{-0.5}$ term in the denominator which makes the rate of adsorption less temperature dependent than the rate of desorption. Thus, the rate of desorption increases faster than rate of adsorption with increasing temperature. This results in less surface coverage of adatoms at higher temperatures. Adsorption is also less at 1 torr than that at 10 torr. Therefore, higher reactant desorption rates may be the reason for very low activation energies at 1 torr [51].

Energies required for surface diffusion of adatoms would be higher at higher coverages, as there is hindering by the neighboring adatoms that needs to be overcome (or more collisions are required to travel the same distance on the surface). Increasing temperature will result in less surface coverage, creating more available pathways for surface diffusion. This in turn increases the deposition rate if surface diffusion plays an important role in the reaction mechanism. Schmitz, et al. [104] found evidence for competitive adsorption of WF_6 and SiH_4 . Partial pressure dependence studies showed that reaction rate is sensitive to SiH_4 pressure ($R \propto P_{SiH_4}^{(1-1.3)}$) while the dependence on WF_6 pressure was zero or minus values ($R \propto P_{WF_6}^{(-0.6-0.0)}$) [7-10]. These partial pressure dependencies consistently observed by several researchers suggest that WF_6 is strongly adsorbed on the W surfaces, making the reaction rate sensitive to SiH_4 partial pressure [143]. This assumption is valid only if adsorption is the rate controlling mechanism as a single elementary surface process step. In summary, SiH_4 partial pressure plays an important role in the surface phenomena.

Gates, et al. [144] have studied the reactive sticking coefficient, S^R , of SiH_4 on the $Si(111)-(7 \times 7)$ surface in a UHV chamber. They measured the sticking coefficients from the H_2 temperature programmed desorption (TPD) area as shown in Figure 53. It was observed that S^R is a combined function of hydrogen surface coverage, θ_H (indicated as H/Si in Figure

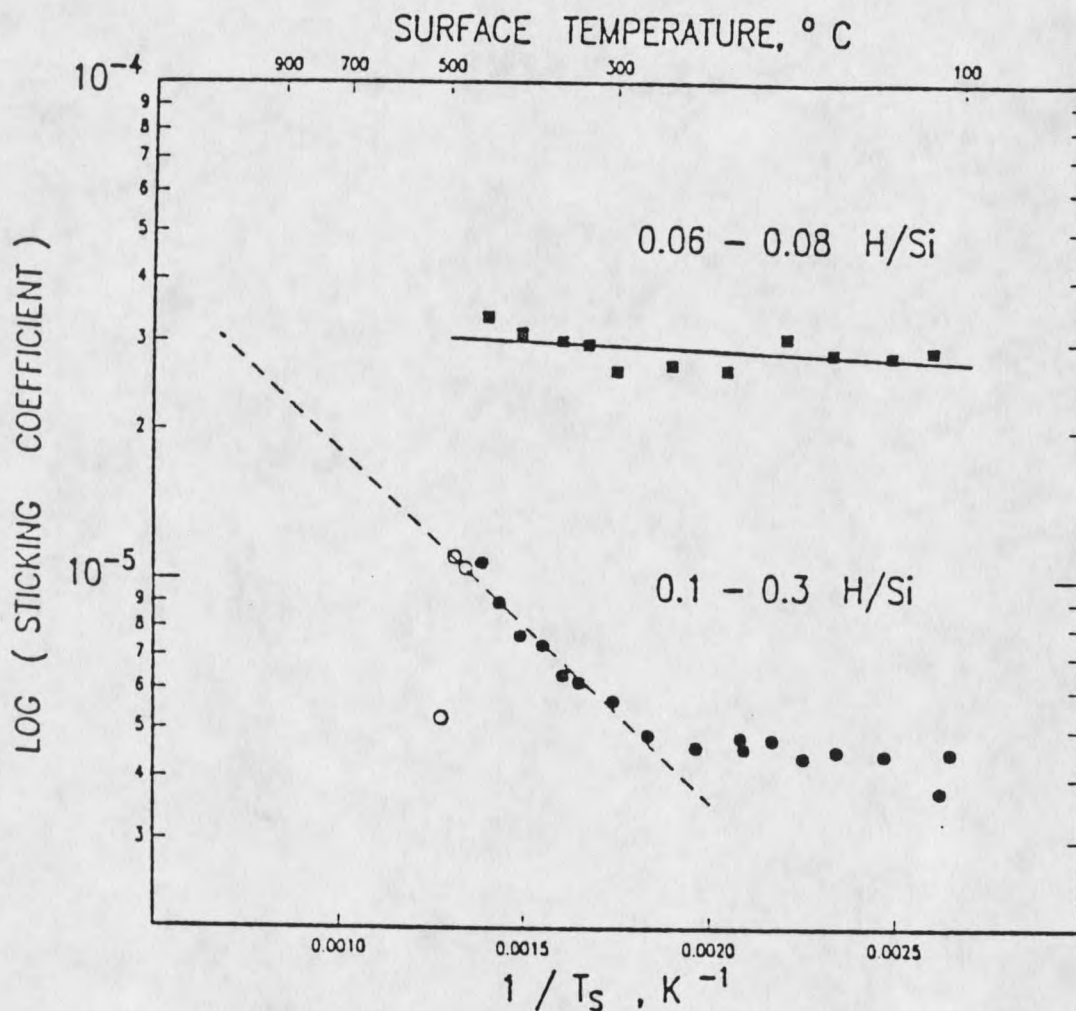


Figure 53. Arrhenius plots from Reference [144] for adsorption of silane on Si(111)-(7x7). The reactive sticking coefficient, S^R was measured as a function of surface temperature, using constant gas exposures and the integral expression $S^R = \text{molecules adsorbed/molecules exposure}$. The fixed gas exposure at 25°C gas temperature were $5.1 \times 10^{-17} \text{ SiH}_4 \text{ cm}^2$ (squares), and $5.5 \times 10^{-18} \text{ SiH}_4 \text{ cm}^2$ (dots). The H atom coverages resulting from the SiH_4 exposure are indicated in the figure.

53), and temperature. For SiH_4 adsorption at very low hydrogen coverages ($\theta_{\text{H}} = 0-0.08 \text{ H/Si}$), the activation energy was 0.007 eV/atom. This essentially zero activation energy suggested that one elementary surface process is controlling the temperature dependence for adsorption on the minority sites. For the higher SiH_4 exposures ($\theta_{\text{H}} > 0.1$), S^{R} is lower and a distinct break in data occurs at 275°C indicating a change in mechanism. This break in the data trend was explained by either of the following:

- (a) A new pathway for adsorption opens at 275°C in which a transition between adsorption dominated by minority and majority sites takes place.
- (b) An additional surface process subsequent to adsorption begins to contribute to the activation energy for S^{R} .

Adsorption behavior of SiH_4 on tungsten surfaces may have some similarities to that on Si(111) surfaces. The low apparent activation energy obtained at 1 torr may be because of the low energy required for SiH_4 adsorption on the reconstructed W(100) surfaces. Surface diffusion of adatoms are also easier on the reconstructed W(100) surfaces, so that it does not contribute to the apparent activation energy. At 10 torr, however, higher surface coverages require additional sites for adsorption, the most probable candidates being sites on W(110) surfaces. This new adsorption pathway may require additional energy. Moreover, adatom surface diffusion on

W(110) surfaces requires more energy than that on the reconstructed W(100) surfaces as discussed before. Surface diffusion of W adatoms on W(110) surfaces give an activation energy of 0.95 eV/atom [145]. This value is higher than the activation energy values measured in this study, indicating that W surface diffusion on W(110) surfaces cannot be a rate determining step. Thus, it appears that the increase in activation energy with higher pressures is a combination of SiH_4 adsorption and subsequent adatom (reactant/reaction intermediate) surface diffusion.

It is suggested that this can be best understood by carrying out temperature programmed desorption (TPD) studies of WF_6 and SiH_4 on single crystal W surfaces. Reactant dissociation products (WF_x and SiF_x) and the reaction intermediates forming on the surface during the reaction can be evaluated by static secondary ion mass spectroscopy (SSIMS) experiments. Tungsten deposition experiments with different SiH_4/WF_6 ratios for the pressure range examined (1-10 torr) would help to understand the mechanism and the degree of competitive adsorption.

Figure 34 shows that the deposition rate changes with reaction time. For 1 torr, the deposition rate increases as the deposition time increases. This is coincident with W(100) domination as the W film thickness increases (increasing deposition time). The activation energy appears to be lower at 10 min reaction times (practically zero as deduced from the

dashed line) than that at 1 to 1.5-min reaction times ($E_a = 0.12$ eV/atom). Thus, higher rates at longer reaction times can be attributed to easier surface diffusion on the reconstructed W(100) surfaces.

For 10 torr, the W deposition rate decreases with increasing deposition times. This is contrary to the trend seen for 1 torr. Films deposited at different pressures show different morphologies as explained before. A continuous film structure is observed at 1 torr, while a porous structure is seen at 10 torr. Film porosity, however, is lost as the aggregates grow larger. This lower porosity observed at longer reaction times decreases the effective reaction surface area and thereby the overall reaction rate. The activation energy is lower for 12-min deposition times than for 1 to 1.5-min deposition times, similar to 1-torr condition. This is evidenced from Figure 34 as the dashed line has a lower slope than does the solid line for 10 torr. The reduction in activation energy for 10 torr with increasing thickness can again be explained by a relative increase in W(100) orientation as the films grow (from 8% to 18% at 385°C in Table 6).

Film Properties

Film Resistivity

Resistivity values presented in Figures 48-50 are only relative values since the film thickness values used are those calculated from the gravimetric, constant-density analysis. SEM cross-sectional and plan-view micrographs show a change in porosity with deposition conditions. Actual film resistivity requires the measurement of the physical film thickness. However, some trends observed in the figures can still be discussed by considering the W film structure and composition.

Figure 48 shows resistivity patterns decreasing in magnitude with increasing thickness. This trend is commonly observed in the literature [10,79,122]. Resistivity is higher for very thin films because the film conductivity at the W-Si interface is mainly characterized by the initial W nucleation. Incorporation of oxygen from the native oxide layer into the W films or segregation of Si atoms from the silicon substrate to the tungsten film surface would increase the resistivity. Oxygen and silicon incorporation were not observed in the W films (by AES analysis). Random orientation of W crystals at the interface is characterized by XRD studies. Each time a conducting electron crosses a grain boundary between two differently oriented crystals, it has to change direction. This straying action increases resistivity. Therefore, random orientation at the interface is expected to give higher

resistivities as opposed to a single-crystal structure. For 1 torr, self-epitaxy is approached at greater thicknesses for which a lower resistivity is expected. However, a dependable comparison cannot be made for very thick tungsten films using sheet resistance data and available SEM cross-sections for physical film thickness because these films are too thick for application of the resistivity formula (Equation 8). The specific resistivity of each W crystal orientation should also be considered as a factor influencing the overall film resistivity.

The change in porosity is another possible reason for the scattering of data in Figure 48. The slopes obtained from Figures 49 and 50 are presented in Table 11. Straight lines in the figures imply a constant resistivity as a result of a consistent structure and impurity concentration throughout the film thickness. Higher slopes indicate higher specific resistivities. Table 11, however, does not show evidence for a decreasing resistivity with increasing temperature as observed by T.Suzuki, et al. [122]. For 10 torr-285°C a distinct decrease in slope after 1.5 min deposition time implies a change in resistivity. SEM micrographs show that this deposition condition gives a very porous structure. The change in porosity seems to be the main reason for the change in resistivity for this condition.

Table 11. Slopes for Sheet Resistance versus Inverse Deposition Time ($t = 0.5-12$ min).

	Slope, ($\Omega/\square$)-min		
	285°C	340°C	385°C
1 torr	255	326	280
10 torr	3,060*	264	330

* $t = 0.5-1.5$ min only, slope changes for longer deposition times.

The $\text{SiH}_4\text{-WF}_6$ literature on W film resistivity is contradictory and does not combine all the possible factors. A detailed study of the W film resistivity is needed; this study must include impurity content, crystal structure and morphology, and must analyze the relative importance of each factor.

Adhesion and Stress

A qualitative discussion of adhesion and stress will be given here. Observations are basically film peeling and the appearance of the films. Adhesion was basically a function of deposition temperature and film thickness. It was a significant problem at the deposition temperatures of 137, 180, 232 and 285°C, especially when the films were thick. Better adhesion was obtained at temperatures higher than 300°C provided that films were not very thick. This observation is

consistent with those of Ohba and Inoue [124] and Rosler, et al. [10]. In addition to the SiH_4 reduction reaction, the Si reduction reaction may occur at high temperatures to a certain extent and contribute to adhesion by forming stronger bonds between W film and Si substrate.

The thermal stress in the W films arises from the difference in the thermal expansion coefficient of Si ($3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and W ($4.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [124]. After deposition at the reaction temperature, the W layer tries to shrink more than Si substrate as the temperature decreases during cool down. This generates stress in the films and the level of stress depends on the temperature and temperature gradients developed within the film. The intrinsic stress, on the other hand, is dependent on thickness, deposition rate, deposition temperature and pressure, and type of substrate used [13]. After peeling from the substrate, curvature of film surfaces is an indication of the type of the stress generated in the film. Tensile stress developed at the W-Si interface causes concave bending, while compressive stress at the interface creates convex bending of the film. A concave bending is observed for the peeling films deposited for 0.5 to 4.0-min reaction times, whereas a convex bending is observed for very thick films deposited for 10 to 12-min reaction times. This change in curvature with increasing tungsten film thickness is in agreement with observations by Ohba and Inoue on films bonded to the substrates [124]. The change in the stress with

thickness seems to be an evidence of a change in film structure with thickness. The SEM cross-sectional view of the W film deposited at 1 torr-285°C condition (Figure 44) is a very good example of such a structural change. Moreover, as discussed earlier, the crystal orientation changes with film thickness. It is known that the structure can expand differently in different directions depending on the type of crystalline structure [146]. Therefore, the change in crystal orientation with film thickness introduces a thermal expansion coefficient changing with W film thickness. Impurities in the films can also contribute to the stress through lattice distortions, inducing structural changes in the films.

SUMMARY AND CONCLUSIONS

Low pressure chemical vapor deposition (LPCVD) of tungsten by SiH_4 reduction of WF_6 was studied in a single-wafer, cold-wall reactor. A temperature range of 137-385°C and a pressure range of 1-10 torr were spanned in the experiments for a SiH_4/WF_6 ratio of 1.0. The thickness of the deposited tungsten was between 300 and 88,000 Å and the deposition rates were between 80 and 9,000 Å/min. Due to sufficient supply of reactants and use of a gravimetric analysis method, it was possible to obtain the rates and the apparent activation energies in the absence of mass transfer effects. In the case of horizontal substrate position and 4-minute reaction times, the apparent activation energies are found to be 0.35 eV/atom for 10 torr, 0.17 eV/atom for 3 torr, and 0.08 eV/atom for 1 torr. The following conclusions are derived from the analysis of the experimental results:

- (1) Different apparent activation energy values for different reaction pressures indicate that the rate controlling mechanism changes with pressure. The higher activation energy observed at higher pressure is deduced to be a result of the limitations in the rate of SiH_4 adsorption and subsequent adatom surface diffusion.

- (2) Tungsten deposition rate is observed to change with the reaction time. This is deduced to be primarily because of the change in W crystal orientation and film porosity with the film thickness. It appears that because of this orientation, the activation energy decreases with thickness.
- (3) The nucleation rate of tungsten on the initial W layer at the W-Si interface appears higher at higher temperatures.
- (4) The lateral growth rate for tungsten aggregates is related to the overall W deposition rate for the reaction times shorter than 1.5 minutes.
- (5) It is suggested that surface mobility of adatoms is higher at higher temperatures and lower pressures and this favors a continuous film growth (2-D).
- (6) For 10 torr deposition conditions, a crystal growth mode resembling the Stranski-Krastanov mode is observed.
- (7) At the W-Si interface, W crystals prefer (110) orientation. This is interpreted to occur due to lack of bonds among neighboring W atoms.

- (8) For high pressures and low temperatures, W(110) preferential orientation persists with W film growth. This is interpreted to be due to easy surface diffusion of adatoms on the atomically smooth W(110) surfaces.
- (9) For low pressures and high temperatures, a W(100) orientation is observed for thick films. W(100) orientation becomes more dominant for thicker films leading to a self-epitaxial growth. This phenomenon is attributed to the reconstruction of W(100) surfaces where the activation energy for adatom surface diffusion is lower on the resulting surface.
- (10) X-ray diffraction (XRD) studies suggest that tungsten aggregates are composed of microcrystals ranging from 140 Å to 290 Å in size.
- (11) Different film thickness uniformities and deposition rates are obtained for the vertical and the horizontal substrate positions. Evidence is presented that this occurs from non-uniform gas ratios and concentrations across the reactor from lack of mixing of the reactant gases inside the reactor and their condensation on the reactor walls.

- (12) Impurity content (Si and F) of the W films deposited under the experimental conditions is below the detectability limit for AES analysis.
- (13) For the 10 torr-285°C deposition condition, film porosity plays an important role in the W film resistivity.
- (14) A good adhesion of the W films to the Si substrate is obtained at deposition temperatures higher than 300°C. At high temperatures, participation of the Si reduction reaction in the SiH_4 reduction mechanism of WF_6 may contribute to the adhesion.
- (15) Film stress changes from tensile to compressive as the tungsten film thickness increases.

CHAPTER 7

RECOMMENDATIONS

In the literature related to film deposition, there is a big gap between the atomistic concepts of crystal growth and measured, bulk deposition kinetics with chemical reaction. In this study, a bridging of this gap is initiated for the SiH_4 - WF_6 reaction system. Almost all of the research in this area is sponsored by industrial concerns to develop specific manufacturing processes. Therefore, the research is fragmentary, mostly targeting short-term results. A comprehensive understanding of the mechanism entails a detailed, long-range study. University-level research seems to be necessary for the mechanism development. The "true" mechanism of the surface reaction can only be understood by using surface science techniques. The following ideas should be useful in understanding the crystal growth mechanism and film quality of W for the SiH_4 - WF_6 system.

- (1) Temperature programmed static SIMS (TPSSIMS) experiments would help reveal the non-desorbing reaction intermediates. A simultaneous residual gas analysis (RGA) would be useful for the identification of gas phase species. These experiments need to be carried out on Si(100) substrates and different W crystal orientations

(e.g., W(110) and W(100)). Competitive adsorption can be elucidated by performing adsorption/desorption experiments at different SiH_4/WF_6 ratios.

- (2) Investigation of the reaction at lower pressures (lower than 1 torr) under differential reactor conditions will supplement the data (rate and morphology data) of this study. Knowledge of W growth trends at lower pressures would lead to a more complete analysis of the mechanism.
- (3) Initial nucleation rates of W on the Si surfaces need to be evaluated by performing experiments for short reaction times (<0.5 min). Understanding of the parameters influencing initial nucleation density of W will increase the control over the morphology and structure of the subsequent crystal layers. Scanning Auger electron microscopy (SAM) and scanning tunneling microscopy (STM) analysis would help evaluate the initial stages of the W nucleation.
- (4) In this study, evidence is found of the dependence of the growth rate on the W crystal orientation. This needs to be explored further by performing deposition experiments on the different single-crystal W surfaces, mainly, W(110) and W(100) surfaces.

- (5) Reconstruction of W(100) surfaces appears to be a function of adsorbate surface coverage in addition to temperature. Surface science studies such as low energy electron diffraction (LEED) with different surface coverages of SiH_4 and WF_6 on single crystal W(100) surfaces would reveal which molecule is more influential in the surface reconstruction process. The incorporation of reflection high energy electron diffraction (RHEED) into the analyses would have a significant contribution in evaluating surface morphology, nucleation and growth kinetics, and surface diffusion.
- (6) Lattice distortions at the Si-W interface can be elucidated by the employment of surface analysis techniques such as LEED and RHEED by designing experiments for the early stages of the W nucleation. The changes in the Si lattice induced by chemisorption can be analyzed by performing submonolayer adsorption studies of WF_6 and SiH_4 on the Si substrate.
- (7) The change in the morphological structure of the growing W crystals in relation to crystal orientation can be illuminated by taking metallographic cross-sections of the thick W films. These micrographs would mark the gross changes in W orientation with thickness.

- (8) Bonding characteristics of the W films on the Si surface can be understood by carrying out soft x-ray photoemission spectroscopy (SXPS) analysis at the Si-W interfaces. Monolayer and submonolayer coverages of W on the Si surface are required in order to get information from the interface. Quantitative measurement of the adhesion strength of the W films to the Si surfaces coupled with XPS analysis would help evaluate the adhesion mechanism. This would provide the parameters to improve the device performance and lifetime.
- (9) In this study, impurity content of the W films is evaluated using Auger electron spectroscopy (AES) only. Other techniques such as secondary ion mass spectroscopy (SIMS) and neutron activation analysis (NAA) are needed for a better resolution of impurity concentration in the films. These techniques are expected to show increased sensitivity to F concentration.
- (10) The $\text{SiH}_4\text{-WF}_6$ literature on the W film resistivity is contradictory and does not combine all the possible factors influencing resistivity. A detailed study of the W film resistivity which includes impurity content, crystal structure, and film morphology is needed.

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APPENDICES

APPENDIX A

Potential Hazards of the Reaction Gases

Potential chemical, fire and explosion hazards of the reactant and product gases are explained in the following paragraphs.

Abbreviations

Threshold Limit Value-Time Weighted Average (TLV-TWA):
The time weighted average airborne concentration of a substance for a normal eight-hour workday or a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (ACGHI 1985-1986).

ACGHI: American Conference of Governmental Industrial Hygienists.

Hydrogen Fluoride (HF)

Hydrogen fluoride is the main corrosive substance as it forms as a product gas from the exposure of tungsten hexafluoride (WF_6) and silicon tetrafluoride (SiF_4) to moist air [147].

Toxicity: Severe exposure of HF causes rapid inflammation and congestion of the lungs. Skin contact with HF develops irritation, burns and severe pain. It can also result in sclerosis of the bones which is the fixation of calcium by fluorine.

TWA: 3 ppm (ACGIH).

Tungsten Hexafluoride (WF_6)

Toxicity: Toxic, irritating and corrosive to tissues, producing burns typical of HF.

TWA: None established. Observation of the TWA of 3 ppm for HF (ACGIH), which forms when WF_6 is hydrolyzed is recommended.

Silicon Tetrafluoride (SiF_4)

Toxicity: Highly toxic, irritating and corrosive to tissues.

TWA: None established. Observation of 3 ppm for HF (ACGIH), which forms when SiF_4 is hydrolyzed is recommended.

Hydrogen (H_2)

Toxicity: Simple asphyxiant.

Fire Potential: Flammable; burns with an almost invisible flame of low thermal radiation. Easily ignited and flame propagates at a rapid rate.

Silane (SiH_4)

Toxicity: Toxic.

TWA: 5 ppm (ACGIH).

Fire Potential: Pyrophoric; however, low concentrations can accumulate without pyrophoric ignition.

Safety in the Reactor System

The reactor system, including the reactant gas cylinders, is placed in an exhaust hood. The electronic control units and the oil filtering system are outside of the hood. The liquid nitrogen trap (see Figure 27) condenses WF_6 , SiH_4 and SiF_4 . During the reaction, reactor outlet gases are diluted with N_2 gas before purging into the hood. After the experiment is completed, air is leaked into the trap while it is still cooled with liquid nitrogen and being pumped down with the roughing pump. This makes condensed WF_6 and SiF_4 hydrolyze gradually. Air is leaked into the trap for 5 minutes at a line pressure of about 10 torr, then the line is brought to atmospheric pressure.

A high velocity SiH_4 leak in a static chamber may not auto-ignite. However, when the gas flow is shut off or a mixing air stream is introduced, the cloud of unreacted SiH_4 may react with explosive violence [148]. The explosion potential of SiH_4 is eliminated by ensuring that the leaking SiH_4 is ignited before it reaches auto-ignition concentrations in air (approximately higher than 2% SiH_4). This is accomplished by maintaining a continuous ignition source at potential leak sites.

APPENDIX B

Calculation of Reactant Fractional Conversion

The highest W deposition rates for the time-dependent experiments are obtained for 1 torr-385°C deposition conditions. Fractional conversion of the reactants are calculated for this reaction condition at which the conversion is maximum. Table 1 shows that the stoichiometric ratio for the W deposition reaction is $\text{SiH}_4/\text{WF}_6 = 1.5$. The employed experimental ratio of $\text{SiH}_4/\text{WF}_6 = 1.0$ suggests that SiH_4 is the limiting reactant, therefore fractional conversion calculations should be based on the SiH_4 concentration. The following assumptions are made for the calculations:

- (1) No condensation on the reactor walls takes place.
- (2) Blanket deposition of W occurs on the Si substrate and the heater surface (area = 5.2 cm x 6.0 cm).

Basis: 1 min of reaction.

$$\begin{aligned}
 \text{Moles SiH}_4 \text{ in} &= (110 \text{ cm}^3) (1.433 \frac{\text{g SiH}_4}{\text{dm}^3}) (\frac{1 \text{ dm}^3}{1000 \text{ cm}^3}) \\
 &\quad (\frac{1 \text{ gmole SiH}_4}{32.12 \text{ g SiH}_4}) \\
 &= 4.90 \times 10^{-3} \text{ mole}
 \end{aligned}$$

(a) At complete conversion ($X_{SiH_4} = 1.0$):

$$\begin{aligned} \text{Moles } W \text{ formed} &= (4.90 \times 10^{-3} \text{ mole } SiH_4) \left(\frac{1 \text{ mole } W \text{ formed}}{1.5 \text{ mole } SiH_4 \text{ reacted}} \right) \\ &= 3.27 \times 10^{-3} \text{ mole} \end{aligned}$$

(b) Experimental:

$$\begin{aligned} \text{Moles } W \text{ formed} &= 5,098 \text{ \AA} \left(\frac{1 \times 10^{-8} \text{ cm}}{1 \text{ \AA}} \right) [(5.2) \times (6.0) \text{ cm}^2] \\ &\quad (19.3 \frac{\text{g } W}{\text{cm}^3}) \left(\frac{1 \text{ gmole } W}{183.85 \text{ g } W} \right) \\ &= 1.67 \times 10^{-4} \text{ moles.} \end{aligned}$$

Then, the fractional conversion is

$$\begin{aligned} X &= \frac{1.67 \times 10^{-4}}{3.27 \times 10^{-3}} \\ &= 0.0511 \end{aligned}$$

A reactant conversion of 5.11% is within the differential reactor conditions (less than 10% conversion).

APPENDIX C

Prediction of Transport Properties for Reaction Gases

Critical properties and molecular weights for the reactant gases are given in Table 12 [147].

Table 12. Critical Properties for Reactant Gases [147].

Gas	Molecular weight, g/mol	T_c , °C	P_c , atm
SiH_4	32.12	-3.46	47.8
WF_6	297.87	177.8	46.3
Ar	39.95	-122.3	48.0

Lennard-Jones parameters can be found from the critical properties by [149]

$$\epsilon / K = 0.77 T_c$$

$$\sigma = 2.44 \left(\frac{T_c}{P_c} \right)^{1/3}$$

where, T_c is in K, and P_c in atm. Table 13 presents Lennard-Jones parameters for the reactant gases.

Table 13. Lennard-Jones Parameters for the Reactant Gases.

Gas	$\epsilon/K, K$	$\sigma, \text{\AA}$
SiH_4	207.55	4.34
WF_6	347.12	5.21
Ar	116.04	3.57

The corresponding transport properties found by using the kinetic theory of monatomic gases at 285°C are given in Table 14.

Table 14. Transport Properties for the Reactant Gases at 285°C.

Gas	KT/ϵ	$\Omega_\mu = \Omega_k$	$\Omega_{D_{AB}}$
SiH_4	2.69	1.069	0.9770
WF_6	1.61	1.279	1.1670
Ar	4.81	0.934	0.8492

APPENDIX D

Reynolds Number Calculation

Reynolds number is defined as

$$Re = \frac{DU\rho}{\mu}$$

where, D is the characteristic diameter of the flow system, U is the linear velocity of the fluid, ρ is the density, and μ is the viscosity. Maximum Reynolds number is obtained at the highest pressure and the lowest temperature operating condition when the system geometry is the same. This corresponds to 10 torr-285°C deposition condition for the vertical substrate position. Gas phase fractions are found from the flow rates as shown in Table 15.

Table 15. Gas Phase Composition of the Reactant Gases.

Gas	Flow Rate, sccm	Fraction, X_i
SiH_4	110	0.3874
WF_6	110	0.3874
Ar	64	0.2252
Total	284	1.0000

Average molecular weight, M_{avg} , for the reactant gases can be calculated from the individual molecular weight of the gases (Appendix C) and their fraction as

$$\begin{aligned}
 M_{avg} &= (0.3874) (32.12 \text{ gSiH}_4/\text{mole}) + (0.3874) (297.84 \text{ gWF}_6/\text{mole}) \\
 &\quad + (0.2252) (39.95 \text{ gAr}/\text{mole}) \\
 &= 136.8 \text{ g}/\text{mole}
 \end{aligned}$$

Average density, ρ_{avg} , is

$$\begin{aligned}
 \rho_{avg} &= \frac{P M_{avg}}{R T} \\
 &= \frac{(10 \text{ torr}) \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) (136.8 \text{ g/mol})}{(82.05 \frac{\text{cm}^3\text{-atm}}{\text{gmole-K}}) (285 + 273 \text{ K})} \\
 &= 3.95 \times 10^{-5} \text{ g/cm}^3
 \end{aligned}$$

Viscosity values for the reactant gases can be approximated with the formula for monatomic gases. Viscosity of a pure monatomic gas may be expressed in terms of the Lennard-Jones parameters σ and ϵ as [149]

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega_\mu}$$

where, μ is in g/cm-s, T in K, σ in Å, and Ω_μ is a function of the dimensionless temperature KT/ϵ (See Appendix C). Then, viscosity values are found as

$$\begin{aligned}\mu_{SiH_4} &= 2.6693 \times 10^{-5} \frac{\sqrt{(32.12)(285+273)}}{(4.34)^2 (1.069)} \\ &= 1.77 \times 10^{-4} \text{ g/cm-s}\end{aligned}$$

and

$$\mu_{WF_6} = 3.13 \times 10^{-4} \text{ g/cm-s}$$

$$\mu_{Ar} = 3.35 \times 10^{-4} \text{ g/cm-s}$$

Since the values are of the same order of magnitude, an average is calculated for the overall viscosity

$$\begin{aligned}\mu_{avg} &= X_i \mu_i \\ &= (0.3874) (1.77 \times 10^{-4} \text{ g/cm-s}) \\ &\quad + (0.3874) (3.13 \times 10^{-4} \text{ g/cm-s}) \\ &\quad + (0.2252) (3.35 \times 10^{-4} \text{ g/cm-s}) \\ &= 2.65 \times 10^{-4} \text{ g/cm-s}\end{aligned}$$

For the vertical substrate position, the characteristic length is the inside diameter of the 6-way cross ($D = 5.61 \text{ cm}$). Then, the Reynolds number is

$$\begin{aligned} Re &= \frac{D U \rho_{avg}}{\mu_{avg}} \\ &= \frac{(5.61 \text{ cm}) \frac{(284 \text{ cm}^3/\text{min}) (1 \text{ min}/60 \text{ s})}{\pi (5.61/2)^2 \text{ cm}^2} (3.93 \times 10^{-5} \text{ g/cm}^3)}{2.65 \times 10^{-4} \text{ g/cm-s}} \end{aligned}$$

$$Re = 0.158$$

APPENDIX E

Sample Calculation for Mass Flux to the Substrate

Mass flux calculations are performed for the vertical substrate position since the gas flow patterns for this position are expected to be less complicated than that for the horizontal position. It is necessary to make assumptions in the calculations since multicomponent diffusion coefficients and partial molal quantities for the components are not known. The molecular weights of SiH_4 and Ar are very close, thus they are assumed to behave similarly in the diffusion phenomena; polarity and geometry effects are assumed negligible. For the sake of simplicity, calculations are based on the diffusion of WF_6 (component A) through SiH_4 and Ar (component B). (For more reliable results, calculations should be based on the diffusion of silane through other gases since SiH_4 is the limiting reactant.) Then, the calculated WF_6 impingement rate on the surface is converted into its equivalent tungsten mass according to the reaction stoichiometry.

The mass diffusivity, D_{AB} , for a binary system at low pressure is given by [149]

$$D_{AB} = 0.0018583 \frac{\sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}}{P \sigma_{AB}^2 \Omega_{D_{AB}}}$$

Lennard-Jones parameters are calculated as (Appendix C)

$$\begin{aligned} \sigma_{AB} &= \frac{1}{3} (3.57 + 4.34 + 5.21) \\ &= 4.37 \end{aligned}$$

and

$$\frac{c_{AB}}{K} = \sqrt[3]{(116.04) (207.55) (347.12)}$$

$$= 202.96$$

Then, at 285°C

$$\frac{KT}{c_{AB}} = 2.34$$

which gives the transport property for mass diffusivity

$$\Omega_{D_{AB}} = 1.0204.$$

Molecular weights are

$$M_A = 297.84 \text{ g/mole}$$

$$M_B = \frac{1}{2} (32.12 + 39.95)$$

$$= 36.04 \text{ g/mole.}$$

Substitution of the values for 10 torr and 285°C into the diffusivity equation gives

$$D_{AB} = \frac{\sqrt{(558)^3 \left(\frac{1}{297.84} + \frac{1}{36.04} \right)}}{(10/760) (4.34)^2 (1.0204)}$$

$$= 16.85 \frac{\text{cm}^2}{\text{s}}.$$

Mass flux of component A, n_A , with respect to stationary axes is given as the summation of diffusive flux $\{j_A\}$ and convective flux $\{\rho_A v_A\}$ as [149]

$$\begin{aligned} n_A &= j_A + \rho_A v \\ &= -\rho D_{AB} \nabla w_A + \rho_A v \end{aligned}$$

where, ρ and ρ_A are densities of gas mixture and component A, respectively; w_A is mass fraction of A; and v is mass average velocity of the gas mixture. Density of WF_6 is

$$\begin{aligned} \rho_A &= (13.28 \frac{g}{dm^3} @STP) \left(\frac{1 dm^3}{1000 cm^3} \right) \\ &\quad \left(\frac{10 torr}{760 torr} \right) \left(\frac{273 K}{558 K} \right) (0.3874) \\ &= 3.31 \times 10^{-5} g/cm^3. \end{aligned}$$

Mass average velocity is

$$\begin{aligned} v &= \frac{(284 \frac{cm^3}{min})}{\pi (5.61 cm^2)} \\ &= 11.49 cm/min. \end{aligned}$$

The gradient of mass fraction, ∇w_A , for one-dimensional diffusion becomes

$$\nabla w_A = \frac{dw_A}{dx}$$

when a linear concentration profile is assumed, it can be written as

$$\begin{aligned}\nabla_{W_A} &= \frac{\Delta W_A}{\Delta X} \\ &= \frac{W_{A_{bulk}} - W_{A_{surface}}}{\Delta X}.\end{aligned}$$

For very fast surface reaction rates, mass fraction of A at the surface is negligible;

$$W_{A_{surface}} \approx 0.$$

Then, the gradient of mass fraction is simplified to

$$\begin{aligned}\nabla_{W_A} &= \frac{W_{A_{bulk}}}{\Delta X} \\ &= \frac{W_A}{\Delta X}.\end{aligned}$$

Mass fraction of WF_6 is

$$\begin{aligned}w_A &= (0.3874) \frac{(297.84 \text{ g } WF_6/\text{mole})}{(136.8 \text{ g gas/mole})} \\ &= 0.84.\end{aligned}$$

Δx is taken as the distance between the reactant inlet and the substrate surface to find the lower limit for the gradient of mass fraction, thus,

$$\Delta x = 10 \text{ cm}.$$

The gradient becomes

$$\begin{aligned} \nabla_{W_A} &= \frac{-0.84}{10 \text{ cm}} \\ &= -0.084 \text{ cm}^{-1}. \end{aligned}$$

Substituting the values in the general flux equation yields

$$\begin{aligned} n_A &= -\rho D_{AB} \nabla_{W_A} + \rho_A v \\ &= - (3.93 \times 10^{-5} \frac{\text{g}}{\text{cm}^3}) (16.85 \frac{\text{cm}^2}{\text{s}}) \\ &\quad (\frac{60 \text{ s}}{1 \text{ min}}) (-0.084 \text{ cm}^{-1}) \\ &\quad + (3.31 \times 10^{-5} \text{ g/cm}^3) (11.49 \frac{\text{cm}}{\text{min}}) \end{aligned}$$

and the flux is

$$\begin{aligned} n_A &= 3.34 \times 10^{-3} \text{ g/cm}^2\text{-min} + 3.80 \times 10^{-4} \text{ g/cm}^2\text{-min} \\ &= (\text{diffusive flux}) + (\text{convective flux}) \\ &= 3.72 \times 10^{-3} \text{ g/cm}^2\text{-min}. \end{aligned}$$

Note that the diffusive flux is one order of magnitude higher than is the convective flux. The theoretical W deposition rate is calculated assuming WF_6 reacts with SiH_4 according to the reaction stoichiometry. For 10 torr-285°C deposition condition, the theoretical deposition rate is

$$\begin{aligned}
 R_{\text{theoretical}} &= (3.72 \times 10^{-3} \frac{\text{gWF}_6}{\text{cm}^2 \cdot \text{min}}) \left(\frac{1 \text{ gmole WF}_6}{297.84 \text{ gWF}_6} \right) \\
 &\quad \left(\frac{1 \text{ mole W formed}}{1.5 \text{ mole SiH}_4 \text{ reacted}} \right) \left(\frac{183.85 \text{ gW}}{1 \text{ gmole W}} \right) \\
 &\quad \left(\frac{1}{19.3 \text{ gW/cm}^3} \right) \left(\frac{1 \text{ \AA}}{10^{-8} \text{ cm}} \right) \\
 &= 7,931 \text{ \AA/min.}
 \end{aligned}$$

APPENDIX F

X-ray Diffraction Line Data for Tungsten Phases

X-ray diffraction lines for the possible tungsten phases are presented in this appendix. The most intense diffraction lines for the experimental analysis range ($2\theta = 30-80^\circ$) are given here; for further data the reader can refer to Reference 33. Values of 2θ are calculated from the Bragg formula (Equation 5) for $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$).

Nomenclature:

hkl : indices for the crystal surface,

d : spacing between the planes,

I/I_1 : intensity ratio based on the most intense peak,

2θ : diffraction angle.

Table 16. X-ray Diffraction Lines for α -W [33].

hkl	$d, \text{ \AA}$	I/I_1	$2\theta, ^\circ$
110	2.238	100	40.26
200	1.582	15	58.27
211	1.292	23	73.19

Table 17. X-ray Diffraction Lines for β -W [33, 115].

hkl	d, Å	I/I ₁	2 θ , °
200	2.52	60	35.60
210	2.25	100	40.04
211	2.06	80	43.91
222	1.45	40	64.17
320	1.40	60	66.76
321	1.34	80	70.17
400	1.26	60	75.37

Table 18. X-ray Diffraction Lines for W₅Si₃ [33].

hkl	d, Å	I/I ₁	2 θ , °
400	2.348	80	38.30
420	2.147	50	42.05
411	2.109	100	42.84
222	2.006	60	45.26

APPENDIX G

Tungsten Crystal Size Calculation

The Scherrer Formula

The Scherrer formula is used to estimate the particle size of very small crystals [31]. The measured width of the diffraction curves are used for the calculations. The Scherrer formula for the particle size, t , is given by

$$t = \frac{0.9 \lambda}{B \cos \theta_B}$$

where, λ is the wavelength; B is the peak width, in radians, measured at half maximum intensity; and θ_B is the angle of incidence. It is known that line broadening due to the natural "spectral width" is proportional to $\tan \theta_B$ and becomes quite noticable as θ_B approaches 90° . Therefore, it is advisable to carry out calculations using diffraction peaks at low diffraction angles to minimize natural line broadening effects. Thus, the diffraction peak for α -W(110) at $2\theta = 40.26^\circ$ is chosen for the calculations.

Sample Calculation for W Crystal Size

Deposition conditions chosen for the sample calculation are:

$T = 285^\circ\text{C}$

$P = 10 \text{ torr}$

$t = 1.5 \text{ min}$

The peak width is given in Table 7 as

$$B = FWHM = 106 \times 10^{-4} \text{ radian.}$$

Substituting B in the Scherrer formula gives the tungsten crystal size as

$$\begin{aligned} t &= \frac{(0.9) (1.54050 \text{ \AA})}{(106 \times 10^{-4} \text{ rad}) \cos(20.13^\circ)} \\ &= 139 \text{ \AA.} \end{aligned}$$

APPENDIX H

SEM Micrographs for Time-dependent Experiments

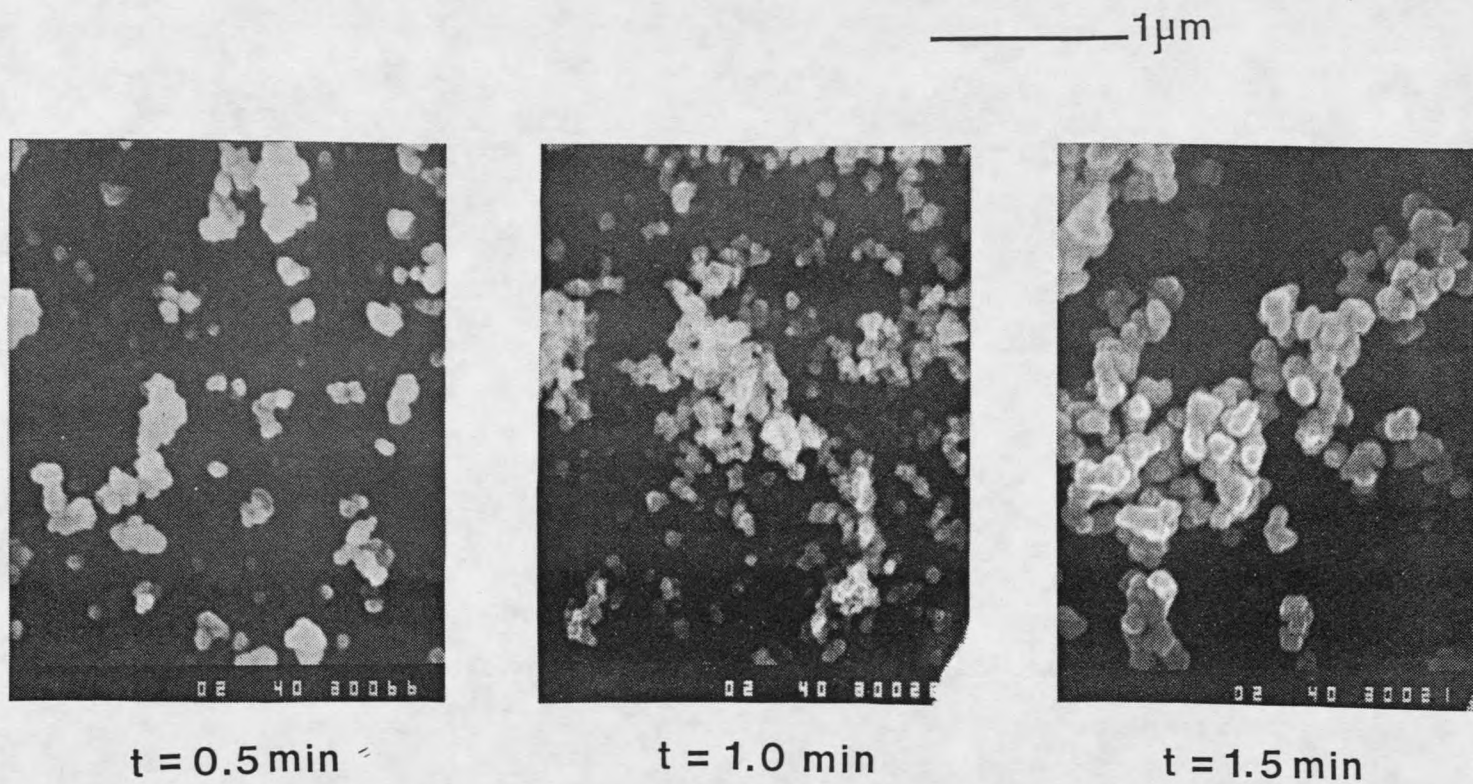


Figure 54. SEM micrographs of W surfaces deposited at different reaction times,
P = 10 torr, T = 285°C.

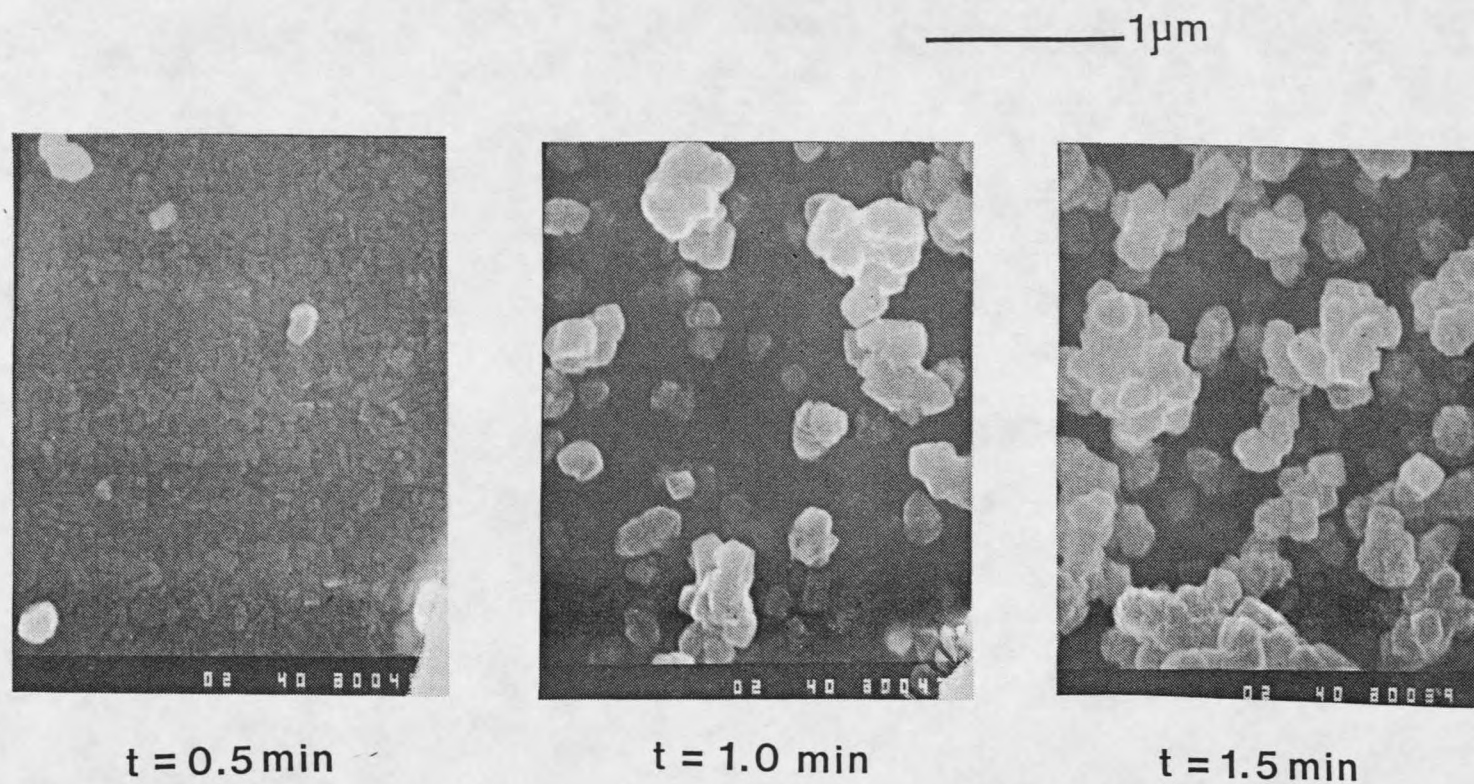


Figure 55. SEM micrographs of W surfaces deposited at different reaction times,
P = 10 torr, T = 330°C.

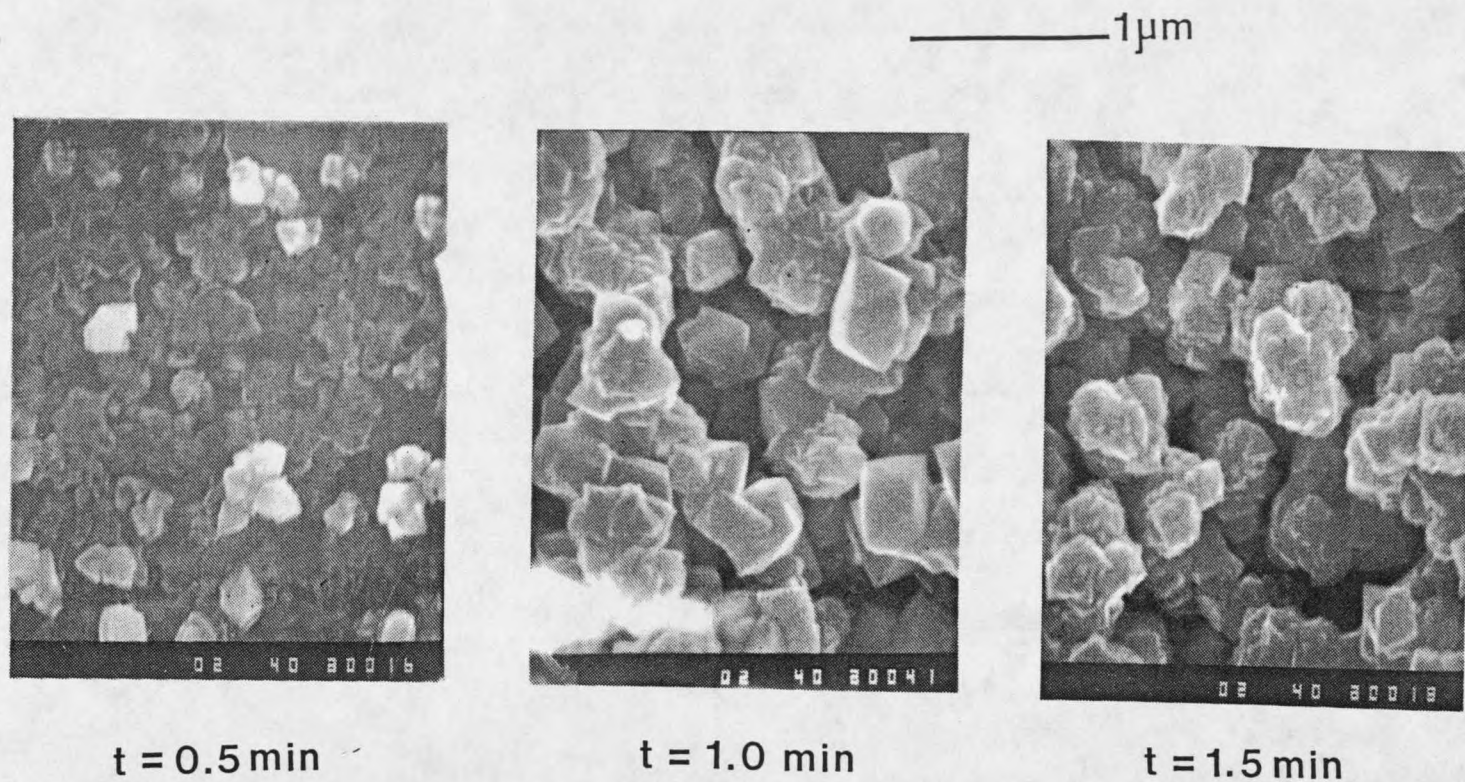


Figure 56. SEM micrographs of W surfaces deposited at different reaction times,
P = 10 torr, T = 385°C.

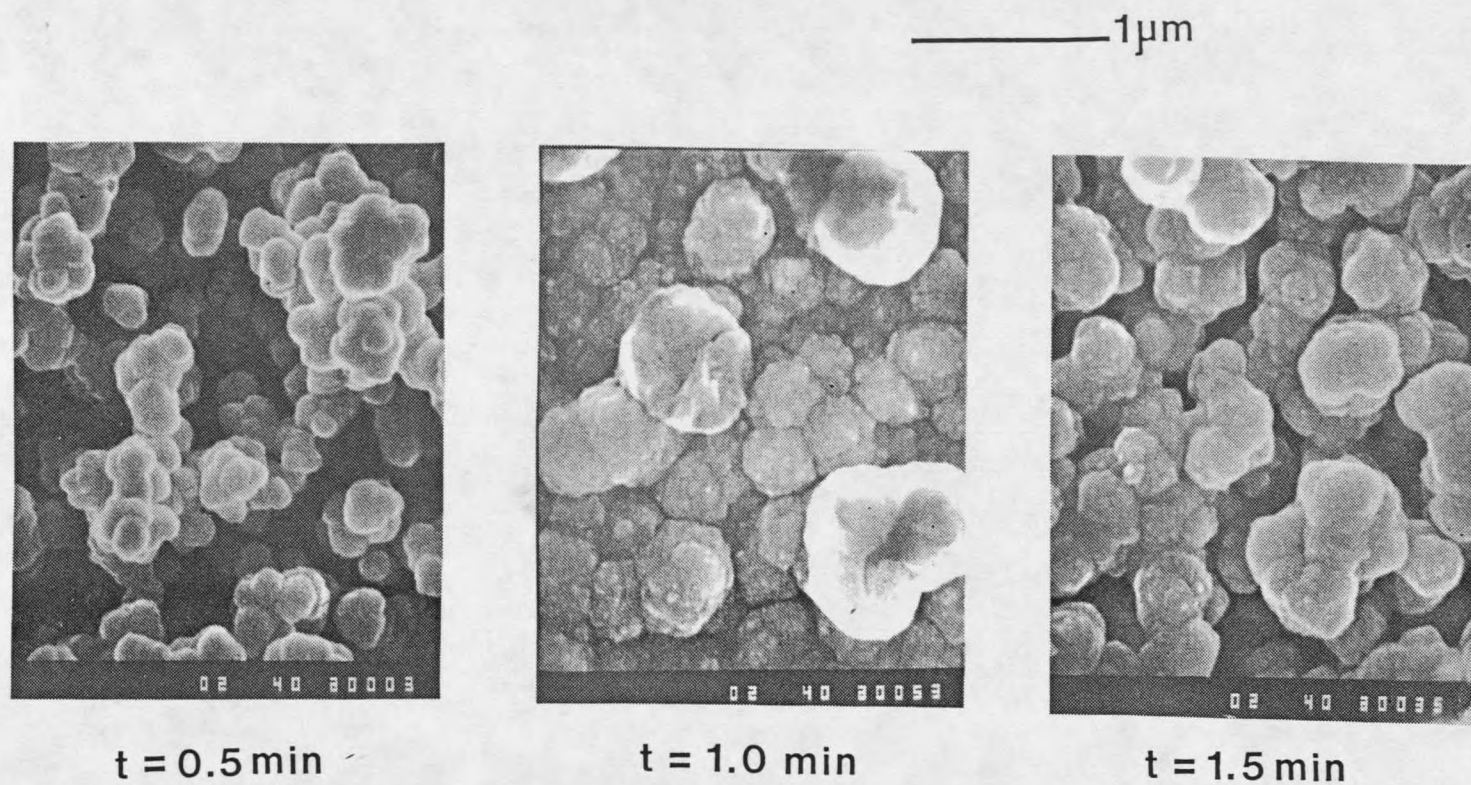


Figure 57. SEM micrographs of W surfaces deposited at different reaction times,
 $P = 1 \text{ torr}$, $T = 285^\circ\text{C}$.

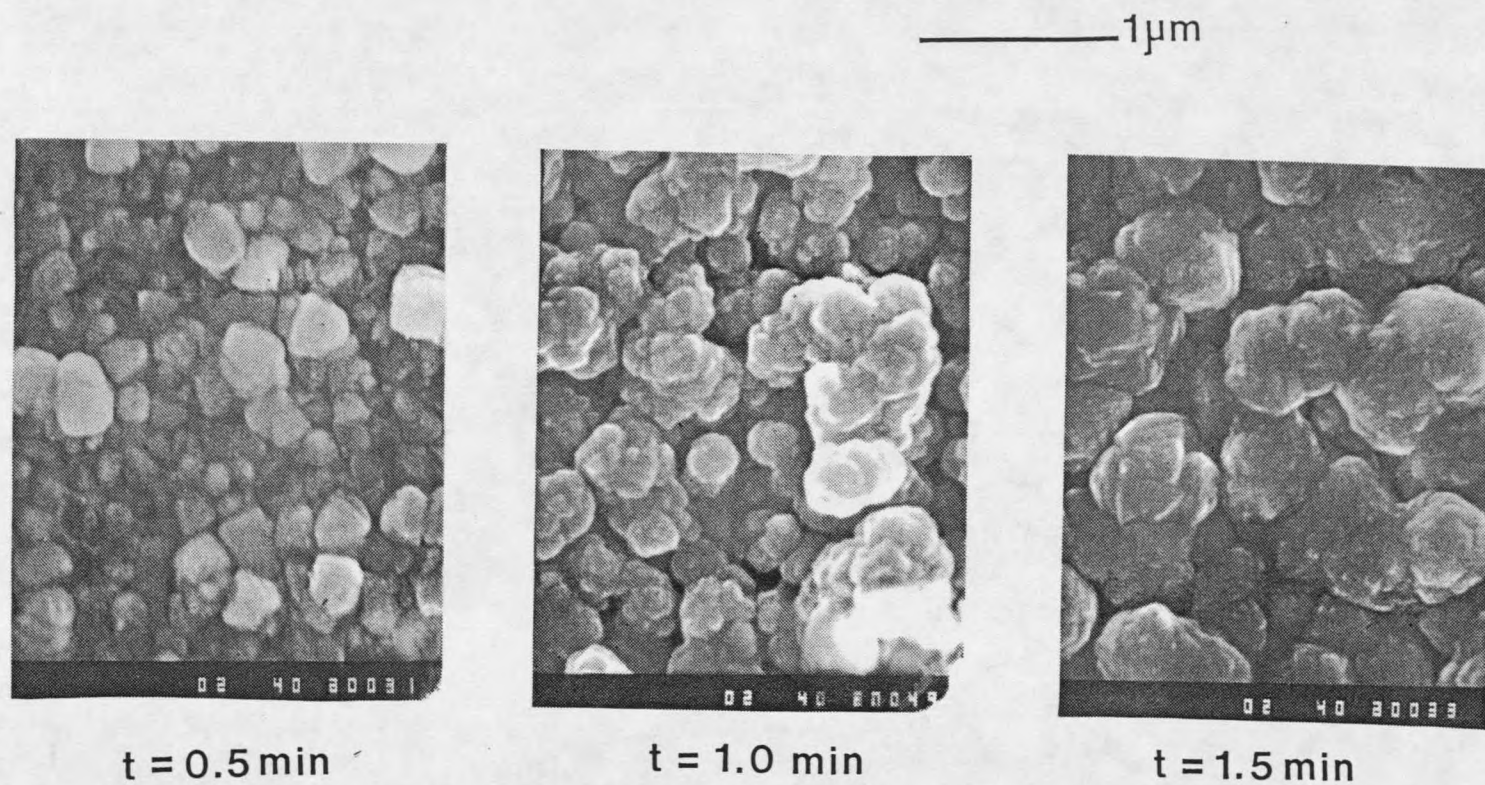


Figure 58. SEM micrographs of W surfaces deposited at different reaction times,
P = 1 torr, T = 330°C.

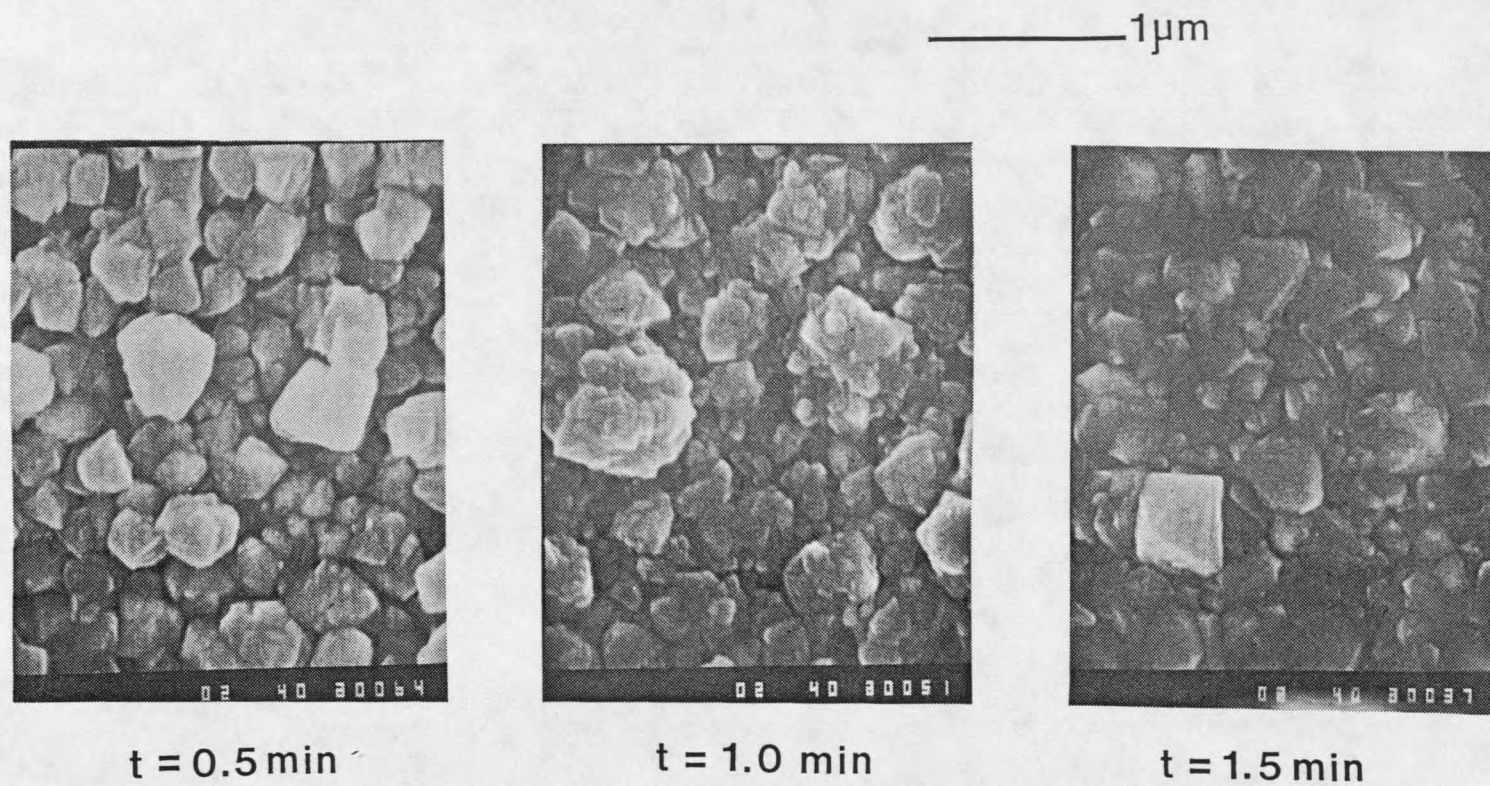


Figure 59. SEM micrographs of W surfaces deposited at different reaction times,
 $P = 1 \text{ torr}$, $T = 385^\circ\text{C}$.

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