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Characterization of low pressure chemical vapor deposition of tungsten thin film

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**CHARACTERIZATION OF LOW PRESSURE CHEMICAL VAPOR
DEPOSITION OF TUNGSTEN THIN FILM**

**A Thesis
Presented to
The Faculty of the Department of
Chemical and Materials Engineering
San Jose State University**

**In Partial Fulfillment
Of the Requirements for the Degree
Masters of Science**

**By
Yelitza Maldonado
Advisor: Gregory L. Young
August 2000**

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ABSTRACT

CHARACTERIZATION OF LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF TUNGSTEN THIN FILM

By Yelitza Maldonado

The low-pressure chemical vapor deposition of tungsten thin films has been characterized by measuring gaseous emissions and deposition rate. Two baseline deposition recipes were characterized: 90 and 300 Torr. Fluorine mass balance resulted in 97.11 and 75.20% respectively. Byproducts identified are unreacted tungsten hexafluoride, silane, hydrofluoric acid, tetrafluorosilane and trifluorosilane. Lower than 100% fluorine mass balance indicated the formation of solid residues in the reactor foreline.

Temperature, WF_6 and H_2 inlet reactant composition effects on deposition rate and emissions were investigated. As temperature increases, the breakdown efficiency of WF_6 increases, that is, more WF_6 dissociates. The deposition rate increases as the WF_6 inlet flow rate increases. Change in WF_6 inlet flow rate (26%) does not have a dramatic effect on the deposition rate (2.2%) as compared to other process parameters. Hydrogen flow rate starts to have an effect on the deposition rate at a critical WF_6 inlet flow rate.

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CHARACTERIZATION OF LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF TUNGSTEN THIN FILM

1. INTRODUCTION

1.1 TECHNOLOGY BACKGROUND

Tungsten is a material widely used in the semiconductor industry. Specifically, it plays an important role in the fabrication of multilevel integrated circuits. Tungsten has the highest melting point (3410 °C) and lowest vapor pressure value of all metals. It has excellent corrosion resistance compared to other materials (Appendix A).

The incorporation and development of tungsten in the semiconductor industry has become important, as the very large system integration (VLSI) complex layouts demanded multilevel connections and very small dimensions. Initially, aluminum was used for simple IC metallization because of its excellent conductivity. The most common aluminum deposition technique is sputtering where the metal is vaporized from solid source by ion bombardment (typically argon ions) and condenses at a cold target (wafer substrate). Sputtering is generally a good deposition technique for large features. However, when trying to fill small gaps or vias, it has very poor step coverage.

As multilevel circuits were developed, the use of aluminum became problematic because of its low melting point (approximately 600 °C). This major drawback placed a constraint on the maximum temperature of all circuit fabrication steps. Another problem with the use of aluminum is its poor step coverage and high electronmigration, which is

the movement of conducting atoms as a result of momentum transfer from current carrying electron (Campbell 412).

Tungsten thin films offer several attractive features as a solution for aluminum drawbacks. First, its high melting point facilitates higher temperature fabrication steps. It has an excellent step coverage and hole fill under optimum process conditions. It has also been shown that it is extremely reliable against electromigration and hillock formation (metal atom accumulation caused by electromigration). Table 1 shows some of the properties of tungsten, aluminum and silicon. In addition, the thermal expansion of tungsten is much more compatible to silicon than that of aluminum. Similar thermal expansion coefficients reduce the formation of contact discontinuities.

	Aluminum	CVD Tungsten	Silicon
Bulk Resistivity	3-4 micro-Ohm-cm	8-10 micro-Ohm-cm	35 micro-Ohm-cm
Electromigration resistance	10^6 Amps/cm ²	$> 10^8$ Amps/cm ²	-
Linear Coefficient of Thermal Expansion Delta L / L C⁻¹	22.5×10^{-6}	4.46×10^{-6}	4.15×10^{-6}
Hillock Formation	Severe	None	N/A
Melting Point	600 C	3410 C	1430 C
Contact resistance at 10^{20} cm⁻³ n-type	5×10^{-6} Ohm cm ²	2×10^{-8} Ohm cm ²	N/A

Table 1. Properties of Tungsten and Aluminum (Brors et al. 1994)

For all these reasons, tungsten is becoming the metal of preference for metal interconnects and vias between metallization layers. Aluminum continues to be the main choice for metal layers primarily because of its low resistivity and well controlled

manufacturing process. Aluminum is also being replaced by copper, a lower resistivity metal, in order to continue increasing the chip speed.

Tungsten can be deposited by the hydrogen or silicon reduction of tungsten hexafluoride. A complete description of tungsten deposition will be discussed later. The simplified scheme of metal layers in integrated circuits is shown in Figure 1.

Figure 1. Multilevel Connections in an Integrated Circuit

One method for depositing tungsten thin film is Low Pressure Chemical Vapor Deposition (LPCVD). During LPCVD processing, reactant gases are introduced into the chamber by a perforated plate (showerhead) in order to assure uniform distribution across the chamber. The chamber is kept at a constant pressure by an automated control system. The reactant gases flow inside the chamber towards the wafer, which rests on a heated susceptor. Molecules diffuse through the stagnant region next to the surface known as

boundary layer. Thermal energy is transferred from the wafer to the reactants driving the deposition reaction. The most common deposition mechanism consists of adsorption of reactants at the wafer surface, dissociation of molecules at the surface, formation of the desired film and desorption of by-products out of the surface. The by-products diffuse out of the wafer region and are pumped out of the chamber. Figure 2 shows a simple schematic of a LPCVD reactor.

Figure 2. Single Wafer LPCVD Reactor

This process is usually performed at low pressure (<760 Torr) and at a temperature range between 350 °C and 600 °C. One of the main advantages of LPCVD compared to atmospheric CVD systems is that operating at low pressure minimizes contaminants adsorbed on the film.

1.2 ENVIRONMENTAL BACKGROUND

In tungsten CVD processes the main byproduct emitted is hydrofluoric acid (HF). HF (CAS number 7664393) is considered a hazardous air pollutant (HAP) defined from the Title III of the Clean Air Act Amendments of 1990. The Semiconductor Industry is seeking the reduction of hazardous chemical and minimization of their environmental impact. Optimization of the tungsten deposition process helps reduce production of HF.

Also, the Environmental Protection Agency has developed an Emission Reduction Partnership for the Semiconductor Industry with details in the Memorandum of Understanding (MOU). The enforcement of the MOU has led to the Semiconductor Industry to quantify the emissions from chip's process fabrication steps (including tungsten depositions). Thus, an important factor in the tungsten thin film deposition characterization is the quantification of all gaseous emissions during the deposition process. The fluorinated compounds that are used by industry subject to this MOU are perfluoromethane (CF_4), perfluoroethane (C_2F_6), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), trifluoromethane (CHF_3) and perfluoropropane (C_3F_8).

NF_3 is used to clean W-CVD chambers after wafer deposition. It is important to minimize chamber deposition for two reasons: to increase the utilization efficiency of W precursors and to minimize PFC emissions (less NF_3 used).

1.3 THESIS OUTLINE

A review of literature work on low pressure CVD of tungsten thin films will be described in Chapter 2. The review will entail choice of precursors, reactions, deposition

mechanisms, reactor issues, and deposition rate. The thesis hypothesis and motivation for this work will be described in Chapter 3. In Chapter 4, experimental procedure including process description, equipment setup, description of analytical techniques and experimental matrix will be described. Data collection and calculations will be given in Chapter 5. In Chapter 6, analysis of baseline deposition processes (90 and 300 Torr) and single variable experiments will be discussed. Finally, overall conclusions and future work are discussed in Chapter 7 and 8 respectively.

2. LITERATURE REVIEW

2.1 REVIEW OF PROCESS KINETICS AND DEPOSITION RATE

Tungsten thin film can be deposited using tungsten hexafluoride WF_6 , WCl_6 and $W(CO)_6$. The first reactant is the most commonly used and will be discussed in more details later. The second choice has not been extensively studied because this chloride compound is a solid at room temperature and needs to be heated to 170 C in order to achieve reasonable vapor pressure (Schmitz 1992). A recent study (Darazoglou et al. 1995) has shown that tungsten can be deposited by the pyrolysis of tungsten hexacarbonyl, $W(CO)_6$. The results indicated that the film had a high carbon and oxygen concentration affecting the film resistivity. Good tungsten films have very low resistivity, close to the aluminum or copper resistivity, and impurities tend to increase it. Reaction chemistry must be optimized before it can be used at a commercial scale.

The most commonly used precursor is tungsten hexafluoride. Depending on the choice of reducing agent and the conditions of the surface where the film is to be deposited, two types of tungsten deposition mechanisms can be performed: blanket and selective deposition. Selective deposition can be achieved by the reaction of tungsten hexafluoride with a silicon surface. Silicon reduces WF_6 as shown in equation (1)

It is selective because WF_6 reacts readily with Si but not with SiO_2 . For patterned wafers, this becomes an advantage to filling contact holes because the film will grow on

silicon contacts but not on intermetal dielectric eliminating the need for etch back step or chemical mechanical polishing to planarize the film.

However, this type of mechanism implies that either WF_6 or Si needs to diffuse through the film in order to react with each other and form a W film. This becomes an issue as the film thickness increases. Diffusion through the film limits the reaction and the deposition rate. Thus, the film is self-limiting and subsequent steps need be performed to continue the film growth. A solution proposed by Shaw et al. (1971) was to add H_2 shortly after the limiting tungsten layer has been deposited. Hydrogen will now be the reducing agent eliminating the need for Si and the reaction can proceed.

Hydrogen reduction of tungsten hexafluoride is the basis for blanket deposition. The reaction goes as follows:

By means of this reaction, tungsten films can be deposited uniformly both on oxide and on silicon regions. However, adhesion is much stronger on silicon than on oxide surfaces. One proposed solution to the weak SiO_2 adhesion is to deposit a thin layer of tungsten silicide before tungsten metallization. Tungsten silicide adheres well on Si and SiO_2 and, if treated well (roughening of the surface by reactive ion etch) W will adhere to the silicide. Tungsten silicide can be deposited by the reaction of WF_6 with silane (SiH_4). In addition, depending on the SiH_4 : WF_6 ratio, one can also grow tungsten films. However, it was found that even for the smallest ratios, silicon contamination results in a large increase in film resistivity (Thomas et al. 1995).

The mechanism of tungsten chemical vapor deposition has been studied for both silicon and hydrogen reduction of tungsten hexafluoride types of chemistries. The first one involves the deposition of selective tungsten by the reduction of tungsten hexafluoride by the silicon surface (Janssen et al. 1992) This type of mechanism is the selective mechanism in which the growth rate is limited by the diffusion of reactants to the interface and subsequent reaction.

In the work done by Janssen, the proposed diffusion mechanism consists of silicon atoms diffusing through the grown tungsten film up to the W-gas interface. Tungsten hexafluoride will then react with the silicon and form solid W and gaseous SiF_4 as the by-product. When the tungsten film is thick enough (approximately 5 nm) for Si to quickly diffuse to the surface, the film growth becomes self-limited. The film growth continues when the reaction is WF_6 gas diffusion limited but slows down when the reaction is Si diffusion limited.

Hayakawa et al. (1998) studied the blanket deposition mechanism. They proposed a simulation of the profile of thin metallic films and tested their model against tungsten film deposition experimental data. This time, tungsten was deposited by the hydrogen reduction of tungsten hexafluoride (blanket deposition). Since these reactants will be used in the development of this thesis, detailed explanation of this model is considered in understanding experimental results.

In Hayakawa's work, the reaction kinetics are not limited by the diffusion of silicon through the W film as explained previously by Janssen, but by the diffusion of the reactants to the wafer surface and surface reactions. The transport effect is described by a

one-dimensional (z-coordinate) Fickian diffusion equation for C, the density of the source gas:

$$-D \frac{dC}{dz} = J \quad 0 < z < \lambda \quad (3)$$

where λ is the boundary layer thickness. The diffusion coefficient is directly proportional to temperature. The concentration of WF_6 at the wafer surface can therefore be described as

$$C(z=0) - C(z=\lambda) = \frac{J\lambda}{D} \quad (4)$$

The surface reactions depend on the tungsten hexafluoride-sticking coefficient to the surface and the reaction of WF_6 (s) to W(s) (where s refers to adsorbed molecule). The number of deposited tungsten molecules per unit area per unit time, r , is given by Equation 5.

$$r = \frac{a \phi}{1 + a \phi S t d} \quad (5)$$

where a is the sticking coefficient, ϕ is the flux density of WF_6 , S is the cross sectional area of the adsorbate and td is the half-value period of the source gas molecule WF_6 on the surface. Hayakawa equated the diffusion flux, J , with the reaction flux, c , assuming a steady state approach and developed the overall growth rate (r) Equation 6:

$$r = \frac{\alpha P_a}{1 + \alpha \beta P_a} \quad (6)$$

where α depends on the sticking coefficient, atomic density and the coefficient of proportion between the partial pressure of WF_6 , P_a , and its flux density, ϕ . The constant β depends on cross sectional area, the decay time and atomic density.

In their experiment, tungsten hexafluoride partial pressure was varied keeping temperature and total pressure constant. The deposition model showed good agreement with the experimental data for three different partial pressures of H_2 as shown in Figure 3. A sticking coefficient of 0.082 was calculated for one of the fitted curves. This value may change according to the adsorption lattice site or the surface condition, such as dangling bonds and terminated with a molecule or an atom. It may also change with temperature at the wafer surface.

Figure 3. Dependence of the growth rate of tungsten films on WF_6 partial pressure. (Hayakawa et al. 1998)

Temperature plays an important role in the transition between a kinetic limited regime and diffusion limited regime in an LPCVD reactor. At low temperatures, the reaction rate becomes too slow due to the exponential dependence of the Arrhenius'

constant and therefore the growth rate is reaction limited. On the other hand, as temperature increases, the reaction rate is greater than mass transport of molecules to the surface, and therefore the deposition rate becomes diffusion limited.

For example, Maeda et al. (1994) investigated the effect of temperature in the deposition of tungsten by the silane reduction of tungsten hexafluoride. They used a water-chilled cold-susceptor LPCVD and ultra high vacuum pressure. Figure 4 shows that the transition between mass transport limited and surface reaction limited occurs at a temperature of 205 °C for the 138 mTorr run and of almost 200 for the 36 mTorr run. The decrease in deposition rate for the lower pressure was explained by the decrease in reactant concentration in the gas phase and therefore fewer precursors are available to deposit the film.

Figure 4. Arrhenius plot of selective tungsten deposition rate. (Maeda et al. 1994)

Deposition Rate

According to Kuijlaars et al. (1995), the kinetic deposition rate can be described by the semi-empirical equation:

$$R_{kin} = c_o [P_{WF_6}]^p [P_{H_2}]^{1/2} \exp\left(-\frac{E_A}{RT}\right) \quad (7)$$

where c_o is an empirical constant, P_{WF_6} and P_{H_2} and the WF_6 and H_2 partial pressures, R the gas constant and T the temperature. At low pressures (10^2 - 10^3 Pa), the constant p can be taken as zero. However, at high WF_6 concentrations, the assumption of zero order kinetics loses its validity.

The deposition process optimization consists of obtaining the desired film properties such as low resistivity, good adhesion and step coverage with high deposition rate. In most cases a tradeoff between quality and productivity needs to be considered especially for selective tungsten deposition since the process is self-limiting.

Kuijlaars performed experiments to test their reaction model on tungsten deposition and the maximum deposition rate achieved was 1200 Å/min. The conditions of operations were: 3 inch wafers, 430 °C, 3 Torr, 7.5×10^{-2} Torr WF_6 partial pressure, 1000 sccm of H_2 and 1200 sccm of Ar. No information on film properties was given.

Table 2 shows a summary of tungsten deposition rates and experimental conditions from different authors. It should be noted in Table 2 that even though Maeda and his colleagues found a high deposition rate (1 micron/min), the maximum thickness grown was only 300 Angstroms. In the case of blanket tungsten, the deposition process needs to be well characterized over a wide range of conditions in order to maximize

deposition rate and throughput. This work will show variable dependence (temperature, pressure and inlet gas ratio) of the deposition and help understand the overall mechanism for future optimization.

Experimental Conditions	Maeda	Hayakawa	Kuijlaars
Deposition Rate(nm/min)	1000	420	1200
Thickness (Angstroms)	< 300	5000	unknown
Reactants Used	WF ₆ /SiH ₄	WF ₆ /H ₂	WF ₆ /H ₂
Mechanism	Selective	Blanket	Blanket
Type of Reactor	Cold Susceptor LPCVD	Cold Wall LPCVD	Cold Wall
Wafer Temp(C) Pressure(Torr)	210 0.006-0.2	450 80	430 3

Table 2. Comparison of literature results.

2.2 REACTOR ISSUES

Different types of reactors have been used to deposit a tungsten thin film. Early work (Shaw and Amick, 1971) on tungsten deposition was done using a simple tubular fused-quartz deposition chamber, with tilted wafer to enhance flow dynamics and therefore uniformity. They used a silicon carbide coated carbon susceptor with a thermocouple inserted at one end. They flowed WF₆ and H₂ for a few seconds through the 700°C heated wafer, and obtained tungsten films with resistivity of 6×10^{-7} ohm-cm $\pm$ 10%.

Gorczyca et al. (1989) studied selective tungsten CVD in a hot wall reactor by silane reduction of WF_6 . The reactor was a 205-cm long quartz tube externally resistively heated. Multiple wafers were loaded vertically in a boat and placed back to back to shield their backside from deposition. The deposition rate was found to be 800 Å/min and the resistivity was around 4×10^{-7} ohm-cm.

Later work was done on single-wafer cold-wall reactors. In 1995, Kuijlaars et al. achieved deposition rates of 1200 Å/min at low pressure (3 Torr). Hayakawa et al. also used cold wall reactors at higher pressures (80 Torr), similar to the reactor used in this work.

In 1998, Colpo et al. investigated the deposition of tungsten thin films by dual frequency inductively coupled plasma assisted CVD. The idea was to both create high-density plasma necessary to obtain metastable phases and to provide an accurate temperature control of the substrate being processed in order to control the microstructure of the deposited film. The maximum deposition rate obtained in their experiment was 5 µm/hr (833 Å/min). The deposition mixture of WF_6 , Ar, and H_2 (1, 20 and 12 sccm, respectively) was introduced in the reactor at a pressure of 3 Pa and temperature of 230 °C.

3. RESEARCH MOTIVATION AND HYPOTHESIS

MOTIVATION:

Most of the LPCVD tungsten thin film effort to characterize the deposition rate has been based on assumed reactions in the gas and wafer surface, mathematical models, reactor conditions and resulting film properties. Quantification of the byproducts resulting from tungsten deposition has become important due to the increasing environmental regulations that the semiconductor industry and the EPA have agreed upon. Also, emissions characterization could be used to characterize the deposition process by comparing the amounts of inlet compounds with the amounts of output compounds, which help determine the validity of existing modeled reactions and efficiency of the reactants.

OBJECTIVES:

The main objective of this thesis is to characterize the low-pressure chemical vapor deposition of tungsten in terms of quantitative emissions of deposition and chamber clean processes and the effect of temperature and inlet reactant flow rate on the deposition growth rate. Also, the relationships between the deposition rate of tungsten films and the gas phase emissions will be investigated.

Tungsten thin films will be deposited using tungsten hexafluoride and hydrogen. Quantitative analysis of the gaseous emission by-products of two baseline processes (90 Torr and 300 Torr) and determination of the deposition rate of tungsten films will be performed. A complete gas phase material balance will be performed including chamber-

cleaning process in order to account for tungsten deposited on the reactor wall during deposition to help close the deposition mass balance.

In the second part of this work, the effect of wafer temperature, WF_6 and H_2 reactant inlet flow rate was also investigated. Single variable experiments around the baseline center points will be performed. Deposition rate and emissions will be investigated in terms of these variables.

4. RESEARCH APPROACH

4.1 EXPERIMENTAL PROCEDURE:

The low-pressure chemical vapor deposition reactor used in the experiment is a commercially available Applied Material's Centura™ platform with a WxZ deposition chamber. The configuration of the WxZ chamber is shown in Figure 5. The WxZ reactor is a cold-wall CVD chamber with a resistively heated susceptor. The inner walls of the reactor are made out of stainless steel. Reactive and inert process gases (WF_6 , H_2 , SiH_4 , and Ar) are uniformly distributed through a perforated plate (showerhead). The systems Proportional-Integral-Derivative (PID) algorithm precisely controls the heater temperature and drives the downstream throttle, which controls the chamber pressure.

Figure 5. Applied Materials' WxZ Reactor Chamber.

A wafer cassette is loaded at the front side of the Centura system, inside the clean room. Silicon wafers, 200 mm in diameter, with a thin layer of titanium nitrate are used in the deposition process. The TiN layer was previously deposited using a MOCVD deposition technique. The TiN layer was deposited to ensure sufficient adhesion of the tungsten film. Each wafer is transported to the single wafer WxZ chamber by an automated transfer blade. The wafer is then ready to be processed. The diagram of the 90 Torr deposition process recipe is shown in Figure 6, which depicts pressure and gas flow rates as a function of time.

Figure 6. Graphical Representation of Typical W film Deposition Recipe

The deposition process consists of two basic steps: W nucleation and W film bulk deposition. During the nucleation step, a very thin layer of tungsten film is deposited by the silane reduction of WF_6 . The main deposition reaction is as follows:

This seed film mechanism speeds up the deposition process because silane reduction of W on TiN proceeds faster than the hydrogen reduction mechanism. Also, it reduces the WF_6 chemical attack on TiN. However, it has poor step coverage which leads to the second type of mechanism used for bulk deposition: $WF_6 + H_2$ (blanket deposition):

Hydrogen is also present during nucleation, however, tungsten reduction has a greater selectivity with silane than with hydrogen. During the bulk deposition step, tungsten hexafluoride is reduced by hydrogen. Argon is used as a diluent to pressurize the chamber when needed. When the deposition is completed, the chamber is purged with Ar and hydrogen, and all gases are pumped out. The wafer is finally removed from the chamber prior to cleaning step.

During the chamber cleaning process, nitrogen trifluoride (NF_3) is flowed through microwave plasma system where it dissociates into a combination of radicals, reactive ions, excited molecules and neutral molecules. All these species flow through a conduit that separates the remote plasma source from the chamber. Fluorine ions attack the tungsten film deposited on the chamber walls producing WF_6 :

Also, as part of the cleaning process, a seasoning step is performed. This seasoning process consists of depositing a thin tungsten film on the chamber walls, in order to remove the excess fluorinated species adsorbed on the chamber walls, and to seal off any loose particles that may contaminate the wafer during the following deposition.

The seasoning process consists of a nucleation step using WF_6 and SiH_4 in excess hydrogen and a bulk deposition step, which uses WF_6 and H_2 as precursors.

During the deposition/clean cycle, FTIR and QMS was used to monitor concentration of species coming out of the CVD reactor as a function of time. By integrating the concentration profiles, the total amount of material can be calculated. By comparing the amount of input gas with the output and the material deposited in the wafer, the mass balance can be closed. Also, after each deposition, the thickness of the W film will be determined using a four-point in-line probe.

4.1.1 EXPERIMENTAL SETUP FOR EMISSIONS CHARACTERIZATION

The experiment was conducted using 200mm silicon wafers with a thin layer of titanium nitride (TiN). Unreacted gases and by-products were pumped out of the reactor through a stainless steel pipe known as the foreline. The sample gas collection port was placed after the exhaust pump. Gases were drawn to the QMS and the FTIR through a 1/8in stainless steel pipe kept at 740 Torr by controlling the pressure with a needle valve. Figure 7 shows the schematics of the experimental setup.

The sampling line was heated to 110 °C in order to drive all the water off the system. The system was purged with nitrogen when no data was collected in order to remove traces of corrosive gases. Detailed description of the theory of Fourier Transform

Infrared Spectroscopy, Quadrupole Mass Spectrometer, and Four-Point In-line Probe techniques will be discussed in detail in the following sections.

Figure 7. Experimental Setup for Emissions Measurements

4.1.2 ANALYTICAL INSTRUMENTATION

4.1.2.1 *Fourier Transform Infrared Spectroscopy*

Fourier Transform Infrared Spectroscopy is a widely used technique for identification and quantification of gaseous, liquid and solid materials. The infrared region is particularly of interest because the natural vibration frequencies of atoms in molecules and crystals fall in the infrared region. Some gas molecules have also rotational frequencies in the far infrared, and some frequencies corresponding to energy levels of electrons in solids and in large molecules are in the near infrared (Parker 1987).

Absorption is a form of interaction between matter and light in which energy exchange is involved. The energy is exchanged if the molecule has an alternating electric field oscillating at the *same frequency* as the moving infrared radiation. Only molecules with a permanent dipole moment have an alternating electric field. Therefore, molecules like N_2 , F_2 , and H_2 can not be detected by an FTIR. The infrared absorption of a molecule is highly characteristic, and often has been referred to as a molecular fingerprint. The infrared spectrum can therefore be used for molecular identification.

Figure 8 shows a simplified scheme of molecular IR absorption.

Figure 8. Fourier Transform Infrared Spectroscopy.

Infrared spectroscopy started to be recognized as early as 1890. In the early 1900s the American physicist W. W. Coblentz determined the infrared spectra of hundreds of substances. However, only after 1940, the development of commercial electronic devices for amplification and rapid data collection allowed extensive use of this technique (Parker 1987).

Quantitative chemical analysis: As previously mention, molecules can be excited to higher vibrational and rotational energy levels by absorption of infrared light. The amount of light absorbed at a certain frequency (or wavenumber cm^{-1}) is related to concentration of molecules in the cell. For non interactive mediums (low concentration gas samples), the amount of light passing though an absorbing medium and the amount of absorber can be related by the Lambert-Beer-Bouguer Law, or simply Beer's law as follows:

$$I = I_o e^{(-kcl)} \quad (11)$$

where I= transmitted intensity
 I_o = initial intersity
 l = pathlength
 k = conversion constant
 c = concentration

Equation 7 can be rewritten as

$$\ln \frac{I}{I_o} = -kcl \quad (12)$$

$$\log \frac{I}{I_o} = \epsilon cl \quad \text{where } \epsilon = k \log e.$$

Absorbance (A) is commonly used and is defined as:

$$A = \log\left(\frac{I}{I_0}\right) \quad (13)$$

A linear relationship between concentration and absorbance is commonly used:

$$A = \epsilon c l \quad (14)$$

Calibration for each of the reactants is usually necessary to calculate the constant ϵ for each component of interest. In this thesis, these calibrations were done by flowing known gas concentrations (approximately 1%) from the calibration box (see Figure 6) diluted with nitrogen. The absorbency of certain peaks of the molecule's adsorption spectrum as a function of gas concentration was determined. Indeed, the integrated area under the peak is the technique commonly used to maximize the signal-to-noise ratio.

Instrumentation: A Nicolet Nexus™ 470 Fourier Transform Infrared Spectrometer was used in the experiment. It consists of a 5-cm gas cell with potassium bromide (KBr) windows and a cooled mercury cadmium telluride (MCT-A) detector. The wavenumber range used in data collection was from 600 to 4500 cm^{-1} . The infrared light source is an Everglow™ source.

4.1.2.2 Quadrupole Mass Spectroscopy: Mass spectroscopy is another technique used for identification of chemical structures, determination of mixtures, and quantitative elemental analysis. Organic and inorganic molecular structure determination is based on the fragmentation pattern of the ion formed when the molecule is ionized. Since such

patterns are distinctive, reproducible and additive, mixtures of known compounds may be quantitatively analyzed. (Parker 1987)

The mass spectrometer consists of mainly three sections: the ion source, the quadrupole and the detector (electron multiplier) as seen in Figure 9. The gas inlet is perpendicular to the page at the ion source section.

Figure 9. Quadrupole Mass Spectrometer.

In the ion source, a tungsten-ruthenium filament is heated to create electrons. Next, the electrons are accelerated by an electric field and bombard the molecules with high energy (70 electron volts). These highly energetic electrons ionize the molecules and create +1, +2 and even +3 charged-ions. The negative ions are attracted to a positively charged plate (repeller) and only the positive ions are directed through a slit, which goes to the quadrupole.

The quadrupole mass filter consists of four metal rods parallel to and at a fixed distance from one another. Opposite rods are connected in pairs to both radio frequency (RF) and direct current (DC). The radio frequency electromagnetic output is a sinusoidal wave of amplitude U and frequency ω . The DC generator output is simply two voltages: $+V$ and $-V$. Solving the complex electric and electromagnetic field differential equations generates a simple linear equation which relates the ion mass-to-charge ratio with either U or V ($m/q = kU$ or $m/q = k'V$). This equation describes the stable ion motion along the z -axis. The stable ion motion of the right m/q will pass through the quadrupole and will be detected at the electron multiplier. The rest of the ions with the different m/q ratio will collide with the rods and never escape the axis. The RF amplitude (U) and DC voltage (V) is varied from 0 to 1200 V and from 0 to 200V respectively in order to scan the m/q ions from 0 up to 800. Some QMS can scan up to 2000 m/q units (Smith 1999).

The electron multiplier (EM) is necessary because the number of ions reaching the detector is extremely small. The EM restores the loss of sensitivity by exploiting the ability of certain surfaces to expel more than one electron when an ion collides with it. The conductive surface of an electron multiplier contains a copper-beryllium surface alloy. The bottom of the EM is grounded so that the electrons are attracted to it. Electrons generated in the last collision with the multiplier surface constitute the signal current output of the multiplier. The signal is sent to an external electronic signal amplification circuit and finally to the data acquisition system. (Smith 1999)

Instrumentation: Mass spectrometer used in the experiment is a UTI Qualitrac IITM analyzer developed specifically to sample corrosive gases at atmospheric pressure and

has a differential pumping system with a dual turbo pump. The software uses the QualiTorr III system integrated in a one-box controller and computer system. Analysis was performed in dynamic mode with a maximum of 10 selected species. The sampling time varies from 3-5 seconds. The electron multiplier was adjusted to provide a signal of 10^{-6} Torr (partial pressure) at AMU 14 (nitrogen). The sensitivity of the instrument is <1 ppm for all detected species in the given conditions.

4.1.2.3 Four Point in-line Probe Technique for Film Thickness

A four-point probe is a technique used to measure sheet resistance. Sheet resistance is the resistance of a square film, that is, the length and the width are the same size. Therefore, if the resistivity (ρ) of the film is known, sheet resistance leads directly to thickness (t) measurements, according to equation 15:

$$R_s = \frac{\rho X}{Xt} = \frac{\rho}{t} \quad (15)$$

For tungsten films, the resistivity is a function of the thickness. The thickness range aimed in this experiment is from 2000 to 5000 Å. From the literature (Appendix B), the resistivity of the tungsten film to be deposited is about $11.5 \mu\Omega\text{-cm}$.

In the four-point probe technique, the four contacts in the probe are located along a straight line at a constant distance s between any two adjacent contacts and the probe is touched to the film. A constant current generator injects a current I into the external contact AA, and voltmeter V measures the difference of potential between the internal contacts. For films with thickness $t \ll s$, the relationship between voltage, current and

sheet resistance is as follows:

$$Rs = 4.53 \frac{V}{I} \quad (16)$$

The pictorial representation of the four-point probe is given in Figure 10. Next, assuming a linear rate, tungsten deposition rate can be calculated by dividing the calculated thickness over the deposition time.

Instrumentation: The sheet resistance measurements for the films deposited in these experiments were performed by an Applied Material's process engineer. The system used was a Varian's Prometrix RS75. The wafer was placed in a automatic system which measured the sheet resistance in 49 points distributed around the wafer. The test diameter for the 200 mm wafers used was 190 mm. Sheet resistance profiles were obtained and the averaged value was used to calculate the deposition rate. Detailed profiles of all wafers tested are given in Appendix C.

Figure 10. Four Point Probe Technique.

4.2 EXPERIMENTAL MATRIX

Figure 11 represents the experimental scheme of the thesis. The experiments are divided in two sections: material balances of 90 and 300 Torr baseline experiments and single variable effect on the deposition rate and deposition emissions: temperature, WF_6 and H_2 inlet flow rate.

4.2.1 EMISSIONS CHARACTERIZATION OF 90 Torr AND 300 Torr W:

First, emissions characterization on the 90 Torr and 300 Torr (baselines) deposition processes was performed. For each process, five deposition runs were recorded for repeatability purposes. Table 3 depicts the experimental deposition conditions

Experiment #	Temperature (oC)	Pressure (Torr)	WF_6 Flow Rate (sccm)	H_2 Flow Rate (sccm)	Time (sec)
1	425	90	95	700	60
2	425	300	250	1000	30

Table 3. Baseline Material Balance Experiments

In addition, since tungsten can also be deposited on the walls of the reactor, a chamber clean process was also included in this analysis. Chamber cleaning is essential to remove any residual films that deposit on the reactor walls and other hardware parts. This hardware deposition becomes an issue because film can flake off the walls, as it grows thicker and can cause contamination of the deposited tungsten film. The clean was also performed once times every 25-wafer pass. Clean emissions on a per wafer basis were calculated dividing each clean process by 25 wafers.

I- Baseline Experiments

II- Single Variable Experiments

Figure 11. Experimental Procedure Flow Diagram.

4.2.2. VARIABLE EFFECT ANALYSIS: MATERIAL BALANCES

For the study of a single variable effect, three process variables will be analyzed: temperature, pressure and inlet gas composition. Table 4 and 5 show the experimental matrix to be performed for temperature and composition variations respectively.

Experiment #	Temperature (°C)	Pressure (Torr)	WF₆ Flow Rate (sccm)	H₂ Flow Rate (sccm)
3	400	90	95	700
1	425	90	95	700
4	440	90	95	700
5	400	300	250	1000
2	425	300	250	1000
6	440	300	250	1000

Table 4. Temperature Experiments

Experiment #	Temperature (°C)	Pressure (Torr)	WF₆ Flow Rate (sccm)	H₂ Flow Rate (sccm)
7	425	90	95	500
1	425	90	95	700
8	425	90	95	1000
9	425	90	120	1000

Table 5. Composition Experiments

Deposition will be carried out at temperatures from 400°C to 440°C and deposition times from 50 to 80 seconds for the 90 Torr deposition process and from 25 to 50 seconds for the 300 Torr deposition process. One wafer will be processed per condition. After each run, thickness will be determined by the sheet resistance technique.

5. EMISSIONS MEASUREMENTS AND DATA ANALYSIS

5.1. CALIBRATIONS

Prior to collecting emissions data, the byproduct gases were calibrated. The gases calibrated were WF_6 , HF , SiF_4 , H_2 , and F_2 . The infrared absorption bands used to quantify the byproducts are given in Table 6, and the compounds analyzed with the QMS with the corresponding AMU are given in Table 7.

Species	WF_6	SiH_4	NF_3	SiF_4	HF
IR region (cm^{-1})	~712	~2190	~910	~1028	~4038
Quant. Method	FTIR	FTIR	FTIR	FTIR	FTIR

Table 6 – Summary of emission species detected with FTIR

Species	H_2	F_2
QMS (AMU)	2	38
Quant. Method	QMS	QMS

Table 7 – Summary of emission species detected with QMS

Calibrations were performed by diluting gas standards with pure nitrogen gas. The standard gases came in a lecture size bottle and were placed inside the calibration system. Silane was calibrated directly from the CVD tool by flowing silane at five different flow rates (300, 200, 100, 50, and 30 sccm). Knowing the nitrogen pump purge, one can calculate the concentration of silane by the following formula:

$$\text{Silane}_{\text{PPM}} = \frac{\text{Silane}_{\text{sccm}}}{\text{Silane}_{\text{sccm}} + \text{Nitrogen}_{\text{sccm}}} * 10^6 \quad (17)$$

The gases were calibrated at concentration range that falls within the experimental conditions. The full set of calibration curves is reported in Appendix D.

5.2. PUMP PURGE CALCULATION

The nitrogen pump purge is necessary to keep the pump running when CVD chamber is idle and to dilute corrosive and toxic gases coming from the CVD tool to concentrations below explosive and flammability limits. This calculation is necessary to quantify emissions measurements on a mass or volume basis. The pump purge was calculated by flowing NF_3 from the tool at various flow rates (100 to 500 sccm). The resulting NF_3 concentration was determined by the previous NF_3 calibration done with the gas standard. The pump purge is then calculated from the following equation:

$$N_{2\text{PumpPurge}(\text{sccm})} = \frac{NF_3(\text{sccm}) \times 10^6}{NF_{3\text{ppm}}} - NF_{3,\text{sccm}} \quad (18)$$

Plotting NF_3 flow rate (from the tool) versus concentration, and assuming that NF_3 flow rate is very small compared to N_2 flow rate, the slope of the linear fit will be $\text{N}_2 \text{ pump purge} / 10^6$. From Figure D-8 in Appendix D, the nitrogen pump purge for the experiment was calculated to be 29935 sccm.

Relaxing the assumption previously done, the percent error of the assumption can be calculated, taking 500 sccm NF_3 as maximum error:

$$\% \text{ error} = \frac{500 \text{ sccm } \text{NF}_3}{500 \text{ sccm } \text{NF}_3 + 29935 \text{ sccm } \text{N}_2} = 1.64\% \quad (19)$$

5.3. DATA COLLECTION

After calibration of all gases and determination of the pump purge, the deposition data was collected and all emissions were quantified. Emissions analysis and data report of deposition and cleaning processes were performed in accordance to the *Equipment Environmental Characterization Guidelines, (Rev. 3.0)*. This protocol describes the guidelines for analyzing and quantifying gaseous emissions using FTIR and QMS instruments. Detailed explanation of analytical methodology is described in Appendix E.

According to the emissions protocol, the following gases should be quantified when using WF_6 , SiH_4 and NF_3 (chamber cleaning gas):

Process Gas	Target Byproducts
WF_6	WF_6 , HF, F_2 , SiF_4 , OF_2 , COF_2
SiH_4	SiH_4
NF_3	NF_3 , HF, F_2 , SiF_4 , OF_2 , COF_2 , NO, NO_2 , N_2O

Table 8. Protocol Target Byproducts

Since oxygen is not present in the deposition process, all oxygen-containing compounds were not quantified. In addition to quantification of gaseous emissions, calculation of volume closure, and breakdown efficiency was performed.

The guideline criterion for successful volume closure on halogens (F, Cl, Br) is >90% closure. If the balance is less than 90%, a plausible explanation must be given (Meyers Rev.3). For example, possible explanations for low mass balance are: solid formation, non-quantified emissions, or liquid emissions. Similarly, silicon and hydrogen balances were calculated by counting the volume of silicon and hydrogen equivalent inlet and outlet.

6. RESULTS AND DISCUSSION

6.1. BASELINE EXPERIMENTS

6.1.1. 90 Torr Tungsten Deposition and Clean Processes:

The main byproducts identified in the FTIR were: unreacted tungsten hexafluoride (WF_6), unreacted silane (SiH_4), hydrofluoric acid (HF), tetrafluorosilane (SiF_4) and trifluorosilane (SiHF_3). All the compounds were quantified except for SiHF_3 due to lack of a calibration standard. The deposition conditions are indicated in Table 9. Note that the first column shows the flows during the bulk deposition step only (Figure 6), however, the total gas flows (second column) are integrated over total recipe time and include stabilization, pressurization and other steps of confidential nature.

Process Conditions	Deposition step only	Total Gas Flow*
Temperature, °C	425	
Pressure, Torr	90	
Time, sec	60	
WF_6 , scc	95	102.5
H_2 , scc	700	4283
SiH_4 , scc	-	30.25

*Table 9. W-CVD Deposition Recipe for 90 Torr process. *Totals flows include stabilization steps and nucleation steps prior to deposition.*

Summary of emissions for the 90 Torr deposition process is shown in Table 10. The total volume out includes the deposition step, nucleation and stabilization steps, hence the presence of silicon containing compounds. Breakdown efficiency is the

percentage of WF_6 that was dissociated during the reaction. Fluorine mass balance represents the percent of fluorine equivalent volume input that comes out of the reactor, or that is accounted for. For a detailed explanation of mass balances and breakdown efficiencies, see Appendix E.

Emissions Compounds	Volume Out (scc)	Breakdown Efficiency %	Fluorine Balance %	Silicon Balance %	Hydrogen Balance %
WF_6	70.03	31.7			
SiH_4	20.39				
SiF_4	2.36				
HF	67.68				
H_2	3714				
F_2	49.95				
Total Emissions	3924.41		97.11	75.21	105.41

Table 10. Emissions and Mass Balance for 90 Torr Baseline Commercial Recipe.

The higher-than 100% hydrogen balance may be due to experimental errors. It must be noted that the silicon balance is lower than 100%. This may be due to the fact that trifluorosilane, which is produced during the nucleation step, was not quantified due to lack of calibration standard.

The FTIR spectrum (Figure 12) depicts the different byproducts detected during the nucleation step and shows the presence of trifluorosilane. Figure 13 shows a typical spectrum for the 90 T deposition process.

Figure 12. Typical FTIR Spectrum during 90 Torr W-CVD nucleation process.

Figure 13. Typical FTIR Spectrum during 90 Torr W-CVD deposition process.

Chamber Clean Process for 90 Torr W deposition: During deposition, a thin tungsten film is also deposited on the wall of the chamber. Chamber cleaning is essential to remove any residual film, which may cause a contamination problem if it flakes off the walls. The cleaning process provides additional insight into the deposition process since it determines how much tungsten is deposited on the walls and other parts of the chamber.

A typical clean process is performed every 25 wafer runs (single wafer), so in order to calculate how much is deposited on each wafer, one must divide the clean emissions by 25. Chamber cleaning was performed after unloading the twenty fifth wafer. The cleaning gas utilized was nitrogen trifluoride, which breaks down by passing through a plasma environment into fluorine and nitrogen radicals and molecules. Fluorine radicals attack the tungsten film producing tungsten hexafluoride. Other predicted byproducts are molecular fluorine, and hydrofluoric acid (HF). The clean time was determined using fluorine as the end point detection method (Raoux et al. 1999).

The chamber clean emissions after 90 Torr W deposition process are shown in Table 11. Equivalent halide is the total volume of fluorine atoms contained in each byproduct. Details are given in Appendix E.

Note that the fluorine volume closure is only 42.83% on the clean process. This may be due to fluorine ions being absorbed by solid formation on the foreline, reducing the amounts that are actually detected. Figure 14 shows the typical spectrum for a NF_3 remote clean after the 90 Torr deposition process.

Emissions Compounds	Volume (scc)	Equivalent Halide, scc	Mass Out g/wafer	Breakdown Efficiency %	Fluorine Balance %
NF ₃ IN	79.6	238.8	0.250		
NF ₃ Out	5.71	17.17	0.0181	92.76	
WF ₆ Out	10.49	62.63	0.1395		
F ₂ Out	10.41	20.81	0.0176		
HF Out	0.453	0.453	0.0004		
Total Emissions	27.06	101.33	0.1756		42.83

Table 11. Emissions during NF₃ Remote Clean after 90 Torr W Deposition Process.

Figure 14. Typical FTIR Spectrum during 90 Torr W-CVD remote clean process.

Seasoning Process after Remote Clean: After each chamber clean process, a chamber “seasoning” step is performed prior to introduction of the next wafer in order to seal off any loose particles that may contaminate the wafer during the following deposition and to prevent contamination of the interface. The seasoning process consists of a nucleation step using WF_6 and SiH_4 in excess hydrogen and a bulk deposition step, which uses WF_6 and H_2 as precursors. The seasoning process recipe is shown in Table 12. A typical spectrum of the seasoning step is shown in Figure 15.

Process Conditions	Seasoning step only	Total Gas Flow, scc*
Temperature, °C	425	
Pressure, Torr	90	
Time, sec	30	
WF_6 , sccm	95	125.83
H_2 , sccm	700	4525
SiH_4 , sccm	-	25

Table 12 –Remote clean seasoning recipe. *Totals flows include stabilization steps and nucleation steps prior to deposition.

Figure 15. Typical FTIR Spectrum of Seasoning Step.

The averaged emissions during chamber clean are shown in Table 13. These emissions occur every 25 wafers. To calculate the emissions on a per wafer basis, reported values must be divided by 25.

Emissions compound	Volume out (scc / wafer)	Equiv. Halide Outlet	Mass Out (g/wafer)	Breakdown Efficiency (%)	Fluorine Balance (%)
WF ₆ IN	125.83	755	1.674	-	-
WF ₆ OUT	73.34	440.01	0.9753	42.67	-
HF OUT	121.86	121.86	1.325	-	-
SiF ₄ OUT	4.477	17.91	0.0526	-	-
SiH ₄ OUT	6.624	-	0.0758	-	-
Total	206.293	579.77	2.429	-	76.79

Table 13. Averaged Process Emissions during Seasoning Process.

6.1.2. 300 TORR TUNGSTEN DEPOSITION PROCESS

The main byproducts identified in the FTIR were: unreacted tungsten hexafluoride (WF₆), unreacted silane (SiH₄), hydrofluoric acid (HF), tetrafluorosilane (SiF₄) and trifluorosilane (SiHF₃). All the compounds were quantified except for SiHF₃ due to lack of a calibration standard. The deposition recipes are indicated in Table 14. Summary of emissions for the 300 Torr deposition process is shown in Table 15.

Process Conditions	Deposition step only	Total Gas Flow, scc*
Temperature, °C	425	
Pressure, Torr	300	
Time, sec	30	
WF₆ , scc	125	132.5
H₂ , scc	50	4950
SiH₄, scc	-	20.25

*Table 14. W-CVD Deposition Recipes: 300 Torr. *Totals flows include stabilization steps and nucleation steps prior to deposition.*

Fluorine mass balance is lower than 100% in the 300 Torr process indicating that the missing fluorine may be contained in solid residues along the foreline or as part of SiF₃H, which was not quantified. Also, it must be noted that the silicon balance is also lower than 100%. Similarly to 90 Torr process, trifluorosilane was not quantified. The FTIR spectra (Figures 16 and 17) depict the byproducts detected during the process.

Emissions Compounds	Volume Out (scc)	Breakdown Efficiency %	Fluorine Balance %	Silicon Balance %	Hydrogen Balance %
WF₆	74.6	43.7			
SiH₄	11.18				
SiF₄	2.62				
HF	52.25				
H₂	4737				
F₂	43.76				
Total Emissions			75.20	68.15	103.93

Table 15. Emissions and Mass Balance for 300 Torr Baseline Recipe.

Figure 16. Typical FTIR Spectrum during 300 Torr W-CVD nucleation step.

Figure 17. Typical FTIR Spectrum during 300 Torr W-CVD deposition step.

Clean process for 300 Torr W deposition: Similarly to the 90 Torr process, the clean process was performed every 25 wafers. Table 16 shows the averaged emissions of chamber cleaning after 300 Torr deposition process.

Emissions Compounds	Volume (scc)	Equivalent Halide, scc	Mass Out g/wafer	Breakdown Effic. %	Fluorine Balance %
NF ₃ IN	78.78	236.32	0.250		
NF ₃	6.27	18.81	0.0199	92.04	
WF ₆	10.82	94.91	0.1439		
F ₂	23.22	46.43	0.0394		
HF	0.452	0.452	0.0004		
Total Emissions	40.76	130.61	0.2035		55.28

Table 16. Emissions during NF₃ Remote Clean after 300 Torr W Deposition Process.

Figure 18. Typical FTIR Spectrum during 300 Torr W-CVD remote clean process.

6.1.3. OVERALL W MASS BALANCES

Overall W mass balances for 90 Torr and 300 Torr were performed including deposition, clean and seasoning. For each pressure, the total mass in and mass out of WF_6 was calculated. The difference between these two masses was assumed to be the mass deposited in each wafer during deposition. The absolute tungsten mass was calculated taking the ratio of the molecular weight of W and WF_6 . The thickness for each process were 3300 Å for 90 Torr and 3000 Å for 300 Torr. Tables 17 and 18 show the balance results.

90 Torr, 3300 Å	Deposition scc	Clean scc	Seasoning scc	Total Volume	Total Mass g	W Mass g
WF_6 IN	102.5	-	5.03	107.53	1.430	0.883
WF_6 OUT	70.03	10.49	2.93	83.45	1.109	0.685
W / wafer						0.198

Table 17. Overall mass balance for 90 Torr deposition process.

300 Torr, 3000 Å	Deposition scc	Clean scc	Seasoning scc	Total Volume	Total Mass, g	W Mass g
WF_6 IN	132.5	-	5.03	137.53	1.829	1.129
WF_6 OUT	74.6	10.82	2.93	88.35	1.175	0.725
W / wafer						0.404

Table 18. Overall mass balance for 300 Torr deposition process.

Note that the mass deposited on the 90 Torr process is less than half of the mass deposited on the 300 Torr process for a higher thickness grown. Fluorine volume closure of the 300 Torr deposition process indicated the possible formation of solids in the foreline and therefore some of the mass may be lost in these deposits, reducing the actual mass per wafer and making it similar to 90 Torr.

6.2. SINGLE VARIABLE EXPERIMENTS

6.2.1. Temperature Effect on the Deposition Emissions

Temperature effect was studied for 90 and 300 Torr processes. For the 90 Torr process, Table 19 describes the recipes used in the temperature experiments and Table 20 shows the corresponding emissions. The heater temperature was varied from 400 °C to 440 °C for both the 90 Torr and the 300 Torr process. The result tables also include the deposition rate for each condition calculated by dividing the thickness by the deposition time.

Deposition Variable Temp. (°C)	Total Emissions Out (scc)				
	WF ₆	SiH ₄	SiF ₄	HF	H ₂
400 (80 sec)	115.16	21.48	2.57	73.16	4868
425 (60 sec)	70.03	20.39	2.36	67.68	3714
440 (50 sec)	50.98	21.08	2.72	75.87	3681

Table 19. Emissions for Temperature Experiment for 90 Torr deposition Process.

Deposition Variables Temp (C)	WF ₆ URE %	Fluorine Balance %	Silicon Balance %	Hydrogen Balance %	DEP. RATE A/min
400	14.2	96.20	79.50	127.5	2547
425	31.7	97.11	75.21	105.41	3287
440	41.2	75.51	78.68	109.15	4443

Table 20. Breakdown efficiency and Mass Balances for 90 Torr W Deposition: Temperature Experiments.

For the 90 Torr process, the higher the temperature (440 °C), the higher the breakdown efficiency (41.8%) indicating that it has not reached a maximum. Hardware limitations did not allow to increase the temperature further to determine whether a

saturation point is reached. This also indicates that the process could be further optimized to increase the deposition rate. Fluorine mass balance is less than 90% for the 440°C condition, which may indicate the acceleration of solids formation in the foreline with temperature.

For the 300 Torr process, the recipes are depicted in Table 21 and corresponding emissions are shown in Table 22.

Deposition Variables Temp. (°C)	Total Emissions Out (scc)				
	WF ₆	SiH ₄	SiF ₄	HF	H ₂
400 (50 sec)	164.21	11.24	2.79	60.74	5474
425 (30 sec)	74.6	11.18	2.62	52.25	4737
440 (25 sec)	79.37	11.16	2.77	54.88	4713

Table 21. Emissions for Temperature Experiment for 300 Torr Deposition Process.

Deposition Variables Temp (°C)	WF ₆ URE %	Fluorine Balance %	Silicon Balance %	Hydrogen Balance %	DEP. RATE A/min
400	23.9	81.63	69.28	111.57	3837
425	43.7	75.20	68.15	103.93	5870
440	28.9	80.92	68.79	105.30	7418

Table 22. Breakdown efficiency and Mass Balances for 300 Torr W Deposition: Temperature Experiments.

Figure 19 . Tungsten Hexafluoride Breakdown Efficiency versus Temperature.

As seen in Figure 19, as temperature increases, the breakdown efficiency increases, that is, more WF_6 is being consumed. The 440 °C point for 300 Torr in Figure 19 could indicate that the deposition rate reached a maximum and the increase in temperature shifts the reaction direction. Another possibility is that temperature and pressure are not independent variables of the breakdown efficiency. However, the deposition rate curve indicates that the rate of reaction is higher as temperature increases (Figure 20).

Figure 20. Deposition Rate vs. Temperature for 90 and 300 Torr W-CVD Processes.

This behavior is consistent with the reaction-limited regime of the Arrhenius' plot. The activation energies for the 90 and 300 Torr tungsten deposition processes were calculated and are shown in Figure 21.

Figure 21. Activation Energy for 90 and 300 Torr Tungsten Deposition Process.

6.2.2. Hydrogen Flow Rate Effect on the Deposition Emissions

The effect of hydrogen inlet flow rate was also analyzed (for 90 Torr process only). The experimental conditions and the resulting emissions for three H₂ flows are summarized in Table 23. The mass balances and deposition rate calculations are shown in Table 24.

Deposition Variables H ₂ (sccm)	Total Emissions Out (scc)				
	WF ₆	SiH ₄	SiF ₄	HF	H ₂
500	82.37	19.82	2.32	76.89	3497
700	70.03	20.39	2.36	67.68	3714
1000	77.05	19.86	2.72	89.46	4037

Table 23. Emissions for 90 Torr W deposition process with varying WF₆ inlet flow rate.

Deposition Variables H ₂ (sccm)	WF ₆ URE %	Fluorine Balance %	Silicon Balance %	Hydrogen Balance %	DEP. RATE Å/min
500	19.6	94.37	73.19	104.35	3916
700	31.7	80.86	75.21	105.41	3287
1000	24.8	91.49	74.64	105.23	4494

Table 24. 90 Torr W-CVD Emissions with Varying Hydrogen Flow.
T= 425 °C, WF₆ = 95 sccm.

Note in Figure 22 that the deposition rate is lowest for the 700 sccm flow of H₂ (3287 Å/min). Comparing the deposition rate with the emissions of the main byproduct, HF, the higher the growth rate, the higher the amount of HF formed and the more WF₆ is utilized, according to the following reaction:

However, at 700 sccm of H_2 , the WF_6 emissions (70.03 scc) are lower than the emissions at 500 sccm H_2 . This trend is not consistent with the reaction indicating that tungsten hexafluoride did not react to make the film but to form possible residues, which are unknown at this point. This trend could also be caused by experimental errors. Further study of this process needs to be performed.

Also, previous studies (Hayakawa) have indicated that hydrogen inlet flow rate starts to have an increasing effect at WF_6 flow rates higher than a critical value (~ 100 Pa for Hayakawas' work). This indicates that the data collected in this experiment may be contained within a no-hydrogen influence regime ($<$ critical WF_6 flow rate) and the differences between values may be due to experimental errors. Determination of the WF_6 critical inlet flow is to be determined.

Figure 22. Deposition Rate, WF_6 and HF emissions as a function of hydrogen flow rate.

At WF_6 flow rates higher than the critical value, the reaction is favored by adding more hydrogen. Similar analysis at higher H_2 flows (2000 and 4000 sccm) was not available at the time, however, previous studies (Lai et al 1999) have shown that the growth rate increases as H_2 inlet flow rate increases.

6.2.3. Tungsten Hexafluoride Flow Rate Effect on the Deposition Emissions

Finally, the effect of tungsten hexafluoride inlet-flow rate was investigated. Table 25 presents the experimental conditions and Table 26 shows the byproduct emissions, including mass balances and deposition rate.

Deposition Variables H_2 (sccm)	Total Emissions Out (scc)				
	WF_6	SiH_4	SiF_4	HF	H_2
95	77.05	19.86	2.72	89.5	4037
120	98.15	20.18	2.53	93.7	4046

Table 25. Experimental Conditions and Emissions of Main Byproducts for WF_6 effect.

Deposition Variables WF_6 (sccm)	WF_6 URE %	Fluorine Balance %	Silicon Balance %	Hydrogen Balance %	DEP. RATE A/min	WF_6 Used scc
95	24.8	91.49	74.64	105.23	4494	25.45
120	23.0	90.55	75.07	105.83	4594	29.35

Table 26. Breakdown efficiencies and Mass Balance for Tungsten Hexafluoride effect.

The deposition rate increases as the WF_6 inlet flow rate increases, as seen in Figure 23. Note that the an increase of 26% WF_6 flow only increases the deposition rate by 2.22 %, indicating that the change in WF_6 inlet flow rate does not have a dramatic effect on the deposition process as compared to other parameters such as temperature or inlet hydrogen.

Figure 23. Deposition Rate, WF_6 and HF emissions as a function of tungsten hexafluoride flow rate.

7. CONCLUSION

In conclusion, the main gas-phase byproducts identified in the 90 and 300 Torr Tungsten deposition processes are unreacted tungsten hexafluoride, unreacted silane, hydrogen, tetrafluorosilane, trifluorosilane, and hydrofluoric acid. These process byproducts confirm the overall blanket deposition reaction:

Higher than 90 % fluorine and hydrogen balance was achieved for the 90 Torr deposition process indicating that all byproducts were accounted for. The less than 100% fluorine balance for the 300 Torr deposition process indicated the presence of solid residues in the foreline which absorb the missing fluorine. Also, all silicon containing species were not accounted for (<90 % mass balance) most probably due to the lack of calibration of trifluorosilane.

Increasing the pressure had an increasing effect in the deposition rate. The high-pressure process (300 Torr) achieved a higher deposition rate (5870 Å/min) compared to the 90 Torr deposition process (3287 Å/min). Also, the higher the pressure, the higher the tungsten hexafluoride breakdown efficiency (31.7 % for 90 Torr vs. 43.7% for the 300 Torr).

During W-CVD chamber clean, the byproducts identified were unreacted NF_3 , molecular fluorine, tungsten hexafluoride and hydrofluoric acid. The high production of fluorine during the remote clean process and the low fluorine mass balance confirmed again the possible formation of solid residues that absorb fluorine radicals. Similar emissions were obtained for the chamber clean after 90 and 300 Torr deposition

processes, indicating that hardware deposition is independent on the process pressure. An average tungsten mass deposited on the wafer after the 90 and 300 Torr processes were 198 mg and 404 mg respectively.

Increasing the temperature increases the deposition rate. This trend was observed for both the 90 and 300 Torr deposition process. The activation energy for 90 Torr process was 0.56 eV. For the 300 Torr process, E_a was found to be 0.68 eV indicating that the energy barrier for the 90 Torr deposition is easier to overcome than that of the 300 Torr process.

Increasing the hydrogen inlet flow rate did not have a significant effect on the deposition rate because the data collected fell within the no effect regime at the WF_6 flow rate investigated. Further experiments need to be performed to determine the critical WF_6 inlet flow at which hydrogen starts to have an influence in the deposition rate.

Finally, increasing WF_6 increases the deposition rate by a small percentage. An increase of 26% in the flow rate only increased the deposition rate by 2.22%.

8. FUTURE WORK

- 1- Identification and quantification of foreline solid residues to account for all fluorine containing species for the 300 Torr W deposition process.**
- 2- Optimization of the deposition process to minimize chamber-cleaning procedures, reducing also the formation of PFCs emitted to the environment.**
- 3- Determination of minimum WF_6 flow rate necessary to characterize hydrogen effect on 90 Torr deposition process.**

9. BIBLIOGRAPHY

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9. APPENDIX

APPENDIX A- PROPERTIES OF TUNGSTEN THIN FILM

Table 1-A Chemical Resistance of Tungsten

Hydrochloric Acid	Resistant to attack
Sulphuric Acid	Resistant to attack
Nitric Acid	Resistant to attack
Aqua Regia-cold	Resistant to attack
Hydrofluoric Acid	Resistant to attack
Caustic Soda, aqueous solution	Resistant to attack
Ammonia to 700C	Resistant to attack
Mercury/Mercury vapor	Resistant to attack
Air/ Oxygen to 400C	Resistant to attack
H ₂ O	Resistant to attack
Hydrogen	Resistant to attack
Nitrogen	Resistant to attack
Carbon Monoxide	Resistant to attack
Ammonia with H ₂ O ₂	Reacts under certain conditions
Carbon Monoxide above 700C	Reacts under certain conditions
Chlorine above 250C	Reacts under certain conditions
Sulphur-molten boiling	Reacts under certain conditions

From [Http://www.tungsten .com/tungcorr.html](http://www.tungsten.com/tungcorr.html)

APPENDIX B- RESISTIVITY VS THICKNESS FOR TUNGSTEN THIN FILMS.

Figure B.1- Room temperature resistivity versus film thickness. (Schmitz 1992)

APPENDIX C-SHEET RESISTANCE PROFILES FOR TEST WAFERS.

The following table identifies each sheet resistance profile with the experimental conditions:

Wafer ID	Temperature	Pressure	WF6 (sccm)	H2 (sccm)
1	425	90	95	500
2	425	90	120	1000
3	425	90	95	1000
4	400	90	95	700
5	400	300	250	1000
6	440	90	95	700
7	440	300	250	1000
SLOT 24	425	300	250	1000
99/10/18 19:18 10	425	90	95	700

Table C-1. Wafer identification for experimental matrix.

Folder ID: 213 Cartridge ID:

Directory No: 6892 File is Sa

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	SHIFT.....	
OPERATOR.....		STATUS 1.....	
PROCESS.....		STATUS 2.....	
EQUIPMENT.....		PROCESS DATE.....	Oct 19, 1999
WAFER ID.....	WFR1	PROCESS TIME.....	18:03
LOT ID.....			
MEAN.....	293.65	WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	22.90 7.799 %	TEST DIAM.....	190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	2.61e+002/3.35e+002	TEMPLATE MAP.....	49 SITE
RANGE.....	73.952	CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	49/ 49	- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0		
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.....	23.0 % C	MEAS TEMP(BF/AF/AVG)	24.5 / 24.4 / 24.4% C
AMPERAGE.....	52.16 mA	VOLTAGE.....	2.998 mV
SORTING SIGMA.....	3.0	MEAN-TARGET.....	0.000
CORRELATION.....	* MOHMS/SQ	-WARNING.....	0.0000 0.000 %
UNITS	OHMS/SQ	-SPEC.....	0.0000 0.000 %
PROMETRIX RS75	ST-6.71		
		PROBE: 1.016 TYPE B	

Tue Oct 19, 1999

18:05

Folder ID: 213 Cartridge ID: Directory No: 6891 File is Saved

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	SHIFT.....	
OPERATOR.....		STATUS 1.....	
PROCESS.....		STATUS 2.....	
EQUIPMENT.....		PROCESS DATE.....	Oct 19, 1999
WAFER ID.....	WFR2	PROCESS TIME.....	18:05
LOT ID.....			
MEAN.....	250.27	WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	23.85 9.531 %	TEST DIAM.....	190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	2.20e+002/3.03e+002	TEMPLATE MAP.....	49 SITE
RANGE.....	82.590	CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	49/ 49	- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0		
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.....	23.0 % C	MEAS TEMP(BF/AF/AVG)	24.5 / 24.4 / 24.5 % C
AMPERAGE.....	61.74 mA	VOLTAGE.....	2.999 mV
SORTING SIGMA.....	3.0	MEAN-TARGET.....	0.000
CORRELATION.....	* MOHMS/SQ	-WARNING.....	0.0000 0.000 %
UNITS	OHMS/SQ	-SPEC.....	0.0000 0.000 %
PROMETRIX RS75	ST-6.71	PROBE: 1.016 TYPE B	

Tue Oct 19, 1999

18:07

Folder ID: 213 Cartridge ID: Directory No: 6894 File in

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	SHIFT.....	
OPERATOR.....		STATUS 1.....	
PROCESS.....		STATUS 2.....	
EQUIPMENT.....		PROCESS DATE.....	Oct 19, 1999
WAFER ID.....	WFR3	PROCESS TIME.....	18:07
LOT ID.....			
MEAN.....	255.90	WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	22.63 8.845 %	TEST DIAM.....	190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	2.28e+002/2.95e+002	TEMPLATE MAP.....	49 SITE
RANGE.....	66.747	CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	49/ 49	- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0		
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.....	23.0 1/2 C	MEAS TEMP(BF/AF/AVG)	24.5 / 24.5 / 24.5 1/2 C
AMPERAGE.....	59.57 mA	VOLTAGE.....	2.997 mV
SORTING SIGMA.....	3.0	MEAN-TARGET.....	0.000
CORRELATION.....	* MOHMS/SQ	-WARNING.....	0.0000 0.000 %
UNITS	OHMS/SQ	-SPEC.....	0.0000 0.000 %

PROMETRIX RS75

ST-6.71

PROBE: 1.016 TYPE B

Tue Oct 19, 1999

18:09

Folder ID: 213 Cartridge ID: Directory No: 6895 File 16 C

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	SHIFT.....	
OPERATOR.....		STATUS 1.....	
PROCESS.....		STATUS 2.....	
EQUIPMENT.....		PROCESS DATE.....	Oct 19, 1999
WAFER ID.....	WFR4	PROCESS TIME.....	18:09
LOT ID.....			
MEAN.....	338.64	WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	24.16 7.136 %	TEST DIAM.....	190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	3.10e+002/3.77e+002	TEMPLATE MAP.....	49 SITE
RANGE.....	67.720	CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	48/ 49	- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0		
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.....	23.0 % C	MEAS TEMP(BF/AF/AVG)	24.6 / 24.5/ 24.5 % C
AMPERAGE.....	43.89 mA	VOLTAGE.....	2.997 mV
SORTING SIGMA.....	3.0	MEAN-TARGET	0.000
CORRELATION.....	* MOHMS/SQ	-WARNING	0.0000 0.000 %
UNITS	OHMS/SQ	-SPEC..	0.0000 0.000 %
PROMETRIX RS75	ST-6.71	PROBE: 1.016 TYPE B	

Tue Oct 19, 1999

18:10

Folder ID: 213 Cartridge ID:

Directory No: 6896 File 16

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	SHIFT.....	
OPERATOR.....		STATUS 1.....	
PROCESS.....		STATUS 2.....	
EQUIPMENT.....		PROCESS DATE.....	Oct 19, 1999
WAFER ID.....	WFR5	PROCESS TIME.....	18:10
LOT ID.....			
MEAN.....	359.69	WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	17.16 4.771 %	TEST DIAM.....	190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	3.36e+002/3.85e+002	TEMPLATE MAP.....	49 SITE
RANGE.....	48.782	CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	49/ 49	- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0		
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.	23.0 % C	MEAS TEMP(BF/AF/AVG)	24.6 / 24.5/ 24.6% C
AMPERAGE.....	36.27 mA	VOLTAGE	2.998 mV
SORTING SIGMA.....	3.0	MEAN-TARGET	0.000
CORRELATION.....	* MOHMS/SQ	-WARNING	0.0000 0.000 %
UNITS	OHMS/SQ	SPEC	0.0000 0.000 %
PROMETRIX RS75	ST-6.71	PROBE: 1.016 TYPE B	

Tue Oct 19, 1999

18:12

Folder ID: 211 Cartridge ID:

Directory No: 6897 File 16

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	
OPERATOR.....		SHIFT.....
PROCESS.....		STATUS 1.....
EQUIPMENT.....		STATUS 2.....
WAFER ID.....	WFR6	PROCESS DATE..... Oct 19, 1999
LOT ID.....		PROCESS TIME..... 18:12
MEAN.....	310.62	WAFER DIAM..... 200.00 mm / 7.87 in
STD DEV.....	21.05 6.776 %	TEST DIAM..... 190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	2.82e+002/3.46e+002	TEMPLATE MAP..... 49 SITE
RANGE.....	63.979	CONTOUR DISPLAY..... STANDARD
# GOOD/SITES.....	48/ 49	- INTERVAL..... 1.000 %
SORTING SIGMA.....	3.0	
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE... * NONE
CORRECT TO TEMP.....	23.0 % C	MEAS TEMP (BF/AF/AVG) 24.6 / 24.6/ 24.6% C
AMPERAGE.....	48.22 mA	VOLTAGE..... 3.001 mV
SORTING SIGMA.....	3.0	MEAN-TARGET..... 0.000
CORRELATION.....	* MOHMS/SQ	-WARNING..... 0.0000 0.000 %
UNITS	OHMS/SQ	-SPEC..... 0.0000 0.000 %
PROMETRIX RS75	ST-6.71	PROBE: 1.016 TYPE B

Tue Oct 19, 1999

18:14

Folder ID: 213 Cartridge ID: _____ Directory No: 6898 File is: 5

TITLE.....	NLT KL 2064 NO BEVEL DEP PREP MARATO	SHIFT.....	
OPERATOR.....		STATUS 1.....	
PROCESS.....		STATUS 2.....	
EQUIPMENT.....		PROCESS DATE.....	Oct 19, 1999
WAFER ID..... WFR7		PROCESS TIME.....	18:14
LOT ID.....			
MEAN.....	372.07	WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	21.76 5.849 %	TEST DIAM.....	190.00 mm / 7.48 in
MINIMUM / MAXIMUM...	3.43e+002/3.98e+002	TEMPLATE MAP.....	49 SITE
RANGE.....	55.533	CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	49/ 49	- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0		
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN	TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.....	23.0 % C	MEAS TEMP(BF/AF/AVG)	24.6 / 24.6/ 24.6% C
AMPERAGE.....	35.39 mA	VOLTAGE.....	2.994 mV
SORTING SIGMA.....	3.0	MEAN-TARGET.....	0.000
CORRELATION.....	* MOHMS/SQ	-WARNING.....	0.0000 0.000 %
UNITS	OHMS/SQ	-SPEC.....	0.0000 0.000 %
PROMETRIX RS75	ST-6.71	PROBE: 1.016 TYPE B	

Tue Oct 19, 1999

17:50

Folder ID: 213 Cartridge ID: Directory No: 6891 File 16

TITLE..... EMISSION 10/19/99
OPERATOR.....
PROCESS.....
EQUIPMENT.....
WAFER ID..... SLOT24
LOT ID.....

SHIFT.....
STATUS 1.....
STATUS 2.....
PROCESS DATE..... Oct 19, 1999
PROCESS TIME..... 17:50

MEAN..... 391.84
STD DEV..... 24.35 6.214 %
MINIMUM / MAXIMUM... 3.63e+002/4.23e+002
RANGE..... 60.227
GOOD/SITES..... 49/ 49
SORTING SIGMA..... 3.0

WAFER DIAM..... 200.00 mm / 7.87 in
TEST DIAM..... 190.00 mm / 7.48 in
TEMPLATE MAP..... 49 SITE
CONTOUR DISPLAY..... STANDARD
- INTERVAL..... 1.000 %

SAMPLE TYPE..... AUTO RANGE-AUTO RUN
CORRECT TO TEMP..... 23.0 % C
AMPERAGE..... 33.25 mA
SORTING SIGMA..... 3.0
CORRELATION..... * MOHMS/SQ
UNITS OHMS/SQ

TEMP. COMP. CURVE... * NONE
MEAS TEMP(BF/AF/AVG) 24.2 / 24.2 / 24.2% C
VOLTAGE..... 2.994 mV
MEAN-TARGET..... 0.000
-WARNING..... 0.0000 0.000 %
-SPEC..... 0.0000 0.000 %

PROMETRIX RS75 ST-6.71

PROBE: 1.016 TYPE B

Mon Oct 18, 1999

19:20

Folder ID: 211

Cartridge ID: G

Directory No: 4450 File 1a 3

TITLE.....	EMISSION TEST MW CLEAN 90 T		SHIFT.....	
OPERATOR.....			STATUS 1.....	
PROCESS.....	BKM8+		STATUS 2.....	
EQUIPMENT.....			PROCESS DATE.....	Oct 18, 1999
WAFER ID.....	99/10/18	19:18 10	PROCESS TIME.....	19:20
LOT ID.....				
MEAN.....	3.4992e-001		WAFER DIAM.....	200.00 mm / 7.87 in
STD DEV.....	32.56 m 9.304 %		TEST DIAM.....	192.00 mm / 7.56 in
MINIMUM / MAXIMUM...	3.07e-001/4.04e-001		TEMPLATE MAP.....	49 SITE
RANGE.....	9.7165e-002		CONTOUR DISPLAY.....	STANDARD
# GOOD/SITES.....	49/ 49		- INTERVAL.....	1.000 %
SORTING SIGMA.....	3.0			
SAMPLE TYPE.....	AUTO RANGE-AUTO RUN		TEMP. COMP. CURVE...	* NONE
CORRECT TO TEMP.....	23.0 % C		MEAS TEMP (BF/AF/AVG)	24.0 / 24.1/ 24.1% C
AMPERAGE.....	103.2 mA		VOLTAGE.....	6.987 mV
SORTING SIGMA.....	3.0		MEAN TARGET.....	0.000
CORRELATION.....	* NONE		- WARNING.....	0.0000 0.000 %
UNITS	OHMS/SQ		- SPEC.....	0.0000 0.000 %
PROMETRIX RS75	ST-6.71		PROBE: 1.016 TYPE B	

APPENDIX D- FTIR AND QMS CALIBRATION CURVES

Figure D-1 WF₆ Calibration Curves Integrated Between 730-688 cm⁻¹

Figure D-2 HF Calibration Curves Integrated Between 4030-4046 cm⁻¹

SiH₄ 1% 5 cm 110°C (08-24-99)

Figure D-3 SiH₄ Calibration Curves Integrated Between 2088-2191 cm⁻¹

SiF₄ 1% 5cm 110°C (10-09-99)

Figure D-4 SiF₄ Calibration Curves Integrated Between 1015-1060 cm⁻¹

Figure D-5 H₂ Calibration Curves obtained with QMS (AMU 2)

Figure D-6 F₂ calibration curve obtained with QMS (AMU 38)

Figure D-7 NF₃ Calibration Curves Integrated Between 866-933 cm⁻¹

Figure D-8 NF₃ Pump Purge Calibration Curve.

Appendix E. Calculations:

A- Mass Balance Calculations (VOLUME CLOSURE)

All experimental data for calculating gaseous emissions was analyzed according to the Equipment Environmental Characterization Guidelines Rev. 3.0 written by Intel, 3M, Air Products and Chemicals, Inc. and NIST. These guidelines are the accepted way to report environmental emissions data.

The mass balance calculation is a comparison of the inlet fluorine-containing compound with the outlet fluorine containing compounds. For example, if 100 sccm of NF₃ were flowed for 60 sec, and 10 scc of CF₄ and 50 scc of HF came out, then the fluorine mass balance is as follows:

$$F - Closure \% = \frac{10scc * 4 + 50scc * 1}{100sccm * 1m * 3} * 100 = 98\%$$

The numerator part of the equation is also known as *Equivalent Halide Outlet* and the denominator as *Equivalent Halide Inlet*. The guideline criterion for success for volume closure is to be greater than 90%. If less than 90%, a possible explanation must be given. For example, possible explanations for low mass balance are: solid formation, unquantitated emissions, or liquid emissions. Similarly, silicon and hydrogen balances were calculated by counting the volume of silicon and hydrogen equivalent inlet and outlet.

The associated error of mass balance is due to emissions volume calculation.

B- Emissions Volume Calculation:

The total emission component volume is calculated by integration of the area under the concentration vs. time curves of each species. For FTIR analysis, a Quant-method was used to convert absorbency vs. time data to concentration vs. time via software program. Next, the integration was performed automatically by the software.

For QMS compounds like Hydrogen and Fluorine, the calibration in Figure B-5 and B-6, were used to convert partial pressure data (raw QMS data) to concentration (PPM). The time-based concentration of each compound was integrated using the following equation:

$$Area_x = \Delta T \sum_{T_o}^{T_{final}} C_x(T)$$

Next, using the pump purge nitrogen flow, and assuming that the total flow rate is the pump purge, the volumetric flow of compound X was calculated using the following equation:

$$C_{xppm} = \frac{FlowRate_x}{TotalFlowRate} * 10^6$$

C- Breakdown Efficiency:

Tungsten hexafluoride breakdown efficiency was calculated using method 2 of the “Equipment Environmental Characterization Guidelines”, as follows:

Method 2 (Plasma and No Plasma):

$$\%Breakdown = 100 * \left[1 - \frac{(Mass)_{grams / wafer_out}}{(Mass)_{grams / wafer_in}} \right]$$

Mass-in refers to the grams of tungsten hexafluoride input calculated from the recipe, and Mass out refers to the integrated volume and subsequent conversion into mass of tungsten hexafluoride out. The error attributed to the mass in and out is 10% accuracy of MFC readings and the standard deviation of the mass out.