Chemical vapor deposition reactor design and process optimization for the deposition of copper thin films

Alan Thomas Stephens

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CHEMICAL VAPOR DEPOSITION
REACTOR DESIGN AND PROCESS OPTIMIZATION
FOR THE
DEPOSITION OF COPPER THIN FILMS

Alan Thomas Stephens II

A Thesis Submitted in Partial Fulfillment
of the Requirements for the Degree of
MASTER OF SCIENCE
in
Mechanical Engineering

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AUGUST 1994
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Alan T. Stephens II
ABSTRACT

A chemical vapor deposition reactor has been designed, built, and optimized for the deposition of copper thin films. The single wafer, stagnation point flow reactor features: six inch substrate capacity; direct metering and vaporization of liquid precursor; reactant introduction into the reactor chamber through a multi-zone precursor injection manifold; optional variable power (0-300W) RF plasma assist; manual loadlock; and, a computer control interface.

Substrate temperature uniformity has been measured to be better than ±1% across the substrate over a wide range of temperatures. The injection manifold was designed for precise tailoring of gas flow characteristics across the substrate, incorporating four concentric, independently adjustable zones, each of which is controlled by a metering valve.

Both Cu(I) trimethylvinylsilane hexafluoroacetylacetone (tmvs hfac) and Cu(II) hfac precursor chemistries have been used. Film properties were determined by four-point probe, surface profilometer, and scanning electron microscope (SEM). The Cu(I) tmvs hfac chemistry yielded the best results with deposition rates exceeding 1000Å/min, average film resistivities below 1.80 μΩ·cm, excellent step coverage, and complete gap fill.
Biographical Sketch

Alan Stephens was born on March 21, 1966 in Rochester, New York, to Alan and Elvira Stephens. He grew up in Rochester where he attended elementary and high school. On September 20, 1984 he enlisted in the United States Air Force where he spent four years and attained the rank of Sergeant. While in the service, he was awarded an Air Force ROTC college scholarship. He completed his undergraduate work at the Rochester Institute of Technology in 1993 with a Bachelor of Science degree in Physics. He continued his education in the field of Mechanical Engineering at RIT, graduating at the top of his class with a Master of Science degree in August, 1994. During the last two years of his undergraduate, and throughout his graduate studies, he was employed as a full-time product development engineer at CVC Products, Inc. It was through this employment that he gained his experience in thin film technology, the subject of this thesis. In September, 1994 the author will leave CVC Products, Inc. and re-enter the Air Force as a Second Lieutenant assigned to the Wright Laboratories at Wright Patterson Air Force Base in Dayton, Ohio.
I begin by thanking those at CVC Products, Inc. who made this thesis possible. First, Christine Whitman and Paul Ballentine for giving me the guidance, financing, and encouragement to pursue this field of research. Second, Tom Omstead for his knowledge and the countless hours of brainstorming we spent together, without which none of this would have been possible. And, finally, Vera Versteeg and Tom Gebo for their many hours of difficult process development work and accurate feedback on reactor performance.

Next, I wish to express sincere gratitude to my thesis advisor, Professor Marietta Scanlon. Her guidance in the writing of this thesis and the time spent talking with me about a myriad of subjects, most often unrelated to this research, is what helped make it more tolerable.

On a more personal note, I thank my parents for their lifelong support of my endeavors and, more specifically, my father for his never-ending advice on all of the important decisions in my life.

Last, and most importantly, I thank my wife Darcie for her love, understanding, and encouragement through this past year when working full-time and attending school full-time left us with very few opportunities to enjoy the finer things in life.
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\( a_{\text{hole}} \)  \( \) injector hole area
\( a_{\text{tot}} \)  \( \) total area of injector holes
\( A_{\text{inj}} \)  \( \) injector tube area
\( C_p \)  \( \) specific heat (constant pressure)
\( C_v \)  \( \) specific heat (constant volume)
\( CF \)  \( \) correction factor
\( d \)  \( \) molecular diameter
\( d_{\text{hole}} \)  \( \) injector hole diameter
\( D \)  \( \) diameter
\( D_{\text{inj}} \)  \( \) injector tube diameter
\( F_{\text{ex}} \)  \( \) exit flow
\( F_r \)  \( \) recycle flow
\( g \)  \( \) acceleration due to gravity
\( h \)  \( \) source to substrate spacing
\( h_L \)  \( \) major head loss
\( h_{\text{tm}} \)  \( \) minor head loss
\( h_{\text{Lt}} \)  \( \) total head loss
\( i \)  \( \) \( \sqrt{-1} \)
\( I \)  \( \) current
\( k \)  \( \) Boltzmann's constant
\( L_e \)  \( \) entrance length
\( L_{\text{hole}} \)  \( \) injector hole length
\( m \)  \( \) mass
\( n \)  \( \) number of mols or injector holes
List of Symbols

P  pressure

\( \Delta P_{\text{plate}} \) pressure drop across injector plate

q  volume flow rate per unit depth

Q  gas flow rate

r  radial displacement

R  substrate radius

Re  Reynolds number

t  film thickness

T  absolute temperature

\( T_{\text{inj}} \) injector temperature

\( \Delta T \) temperature change/difference

v  velocity

\( v_r \) radial velocity

\( v_\theta \) angular velocity

\( v_z \) vertical velocity

V  voltage

\( x_i \) molar fraction

z  vertical distance

\( \beta \) gas expansion coefficient

\( \delta_s \) boundary layer thickness (substrate)

\( \delta_w \) boundary layer thickness (reactor wall)

\( \phi \) angular displacement
List of Symbols

\( \gamma \)  ration of specific heats \( (C_p/C_v) \)
\( \Gamma \)  liquid flow rate
\( \lambda \)  mean free path
\( \Lambda \)  solid flow rate
\( \mu \)  viscosity
\( \mu_s \)  source flow strength
\( \mu_{tot} \)  complex viscosity
\( \theta \)  divergence angle
\( \rho \)  density or resistivity
\( \rho_{tot} \)  complex density
\( \nu \)  kinematic viscosity
\( \omega \)  angular velocity
\( \Omega \)  complex velocity potential
The deposition of thin film metallization layers has become quite commonplace in many of today's industrial products. Costume jewelry, trophies, children's toys, and other miscellaneous items represent just a few examples of some of the less sophisticated applications of these thin films. However, the more sophisticated applications of this vacuum technology are not quite as obvious, the most prevalent examples of which are microchips.

Since thin films are produced in a vacuum environment, it seems worthwhile to cover the basics of vacuum technology before proceeding much further. A vacuum region can be described as a space from which all matter has been removed. The pressure in this reference space would be zero absolute in any system of pressure measurement (a physical impossibility). The introduction of gaseous molecules into this space will increase the pressure linearly with gas density and temperature according to the ideal gas law.

In the SI system of units, pressure is measured in Pascals \((N/m^2)\). However, in the vacuum industry, the standard reference is the Torr, named after Torricelli who invented the barometer. Atmospheric pressure, which is \(1.013 \times 10^5 \) Pa, will support a 760 mm column of mercury and is equivalent to 760 Torr.
1. Introduction

There are several other important aspects related to the level to which one obtains a vacuum environment. The mean free path, $\lambda$, is the average distance a molecule will travel before colliding with another molecule and is highly pressure dependent. Additionally, the viscosity of a gas in a vacuum system is also highly pressure dependent. If the pressure is such that a gas molecule will collide with another gas molecule before colliding with its surroundings, then the gas will exhibit "viscous flow." If, however, the gas collides more often with its surroundings than other gas molecules, then the flow type is called "molecular flow."

These pressures are dependent upon the system geometry making it difficult to define a particular cut-off point for each type, but typical values are:\textsuperscript{1}

- Viscous Flow: 100 mTorr to 50 Torr
- Molecular Flow: 0 Torr to 10 mTorr

The region of pressure between 10 and 100 mTorr is where the transition between molecular and viscous flow occurs. Therefore, the flow exhibits characteristics of both types and is somewhat more difficult to classify.
Now that the very basic foundation of vacuum science has been established, it is possible to address the issue of thin film deposition of metals for the semiconductor industry. Metallization layers and multilevel interconnects are becoming more important to the semiconductor industry than ever before. This is primarily due to the requirements of high speed and reliability at the component level within microchips. This high speed and reliability is obtained by using a process maximizing deposition rate, step coverage, and film uniformity while simultaneously minimizing the resistivity, impurities, stress, and electromigration of the deposited material. Additional parameters of interest are the grain size and reflectivity of the deposited film.

Traditional physical vapor deposition (PVD) technology (usually sputtering) is incapable of providing adequate step coverage for high aspect ratio substrates while simultaneously producing uniformly deposited films. In response to this inadequacy, processes involving Metal Organic Chemical Vapor Deposition (MOCVD) have been developed for the deposition of copper and other metals of interest for the semiconductor industry. However, these processes are much more complex than PVD techniques.

The Chemical Vapor Deposition (CVD) processes of interest here involve both Thermal CVD and Thermal Plasma
Assisted CVD (PACVD) of a metal organic precursor containing copper. The copper is liberated from its precursor carrier and selectively deposited onto the substrate with excellent resistivity, gap fill, and uniformity characteristics (once the process has been optimized). To achieve this goal it is necessary to design a vacuum reactor, substrate heater, and precursor injection manifold which offer excellent gas flow characteristics and process flexibility. Once done, the process parameters themselves must be optimized to attain the desired film properties as previously described.

As the demand for more densely packed micro-devices continues to grow, substrates with higher aspect ratios (as evidenced by decreasing line widths) become necessary. Therefore, the requirement for reliable metal interconnects for semiconductor devices increases. This thesis will focus on the work being done to develop a CVD process capable of producing copper films with near bulk resistivity and other optimized parameters of interest.

Accomplishment of this task will involve: the assembly of a CVD vacuum deposition reactor; a literature search on both reactor design and the process of thermal CVD of copper; a comprehensive analysis of the CVD precursor injection manifold design which will include mathematical
modeling; and finally, evaluation and optimization of the copper thin films produced by the reactor.

There are several manufacturers of CVD equipment and just as many different injector designs. This is mostly due to the injector's extreme importance to the entire process and to avoid patent infringement. The injector designed in this thesis will be primarily based upon mathematical modeling, the designs of other equipment manufacturers, and its ability to deliver the precursor as required. Additionally, its overall reliability, particle generation characteristics, and cost of manufacturing/ownership will be taken into consideration.

Last, but certainly not least, is the actual production, evaluation, and optimization of the copper thin films. Based upon the process results obtained, several modifications to the precursor injector itself may be required.
2. Literature Review

2.1. CVD Reactor Configurations

The process of chemical vapor deposition (CVD) to deposit thin films of insulators, semiconductors, and metals has become one of the most important techniques for thin film deposition in today's microelectronics industry. The process is carried out by introducing a chemical precursor, containing the material to be deposited, into the reactor in a gaseous state. The material of interest is then liberated from this precursor carrier and selectively deposited onto the substrate.

Electronic devices are becoming much more sophisticated and in recent years, circuit designers have reduced circuit features to dimensions of 1 μm or less. Hence, current designs of CVD reactors are being pushed to their limits as evidenced by more stringent tolerances with regard to film properties than ever before. As one example, where older circuits could tolerate a variation of film thickness uniformity of ±5% over a 100 mm substrate diameter, newer circuits require ±1-2% uniformity over 150 mm substrates. An even greater challenge presents itself as the semiconductor industry becomes more interested in 200 mm substrates with the same deposition specifications.2-3
2. Literature Review

Traditional CVD reactor designs were built without a great deal of concern for the actual process dynamics occurring inside the reactor and then optimized through an experimental trial and error approach. However, this method has become increasingly more difficult and prohibitively expensive. As a result, reactor designers have begun creating mathematical models of the processes occurring within the reactor taking into account both reactor geometry and process kinetics. Provided the mathematical model is an adequate representation of the entire system, the reactor can both be designed and optimized on a computer.

There are several different reactor configurations which are either currently in use or being experimented with. These reactor types include (but are not necessarily limited to) the following: multiple wafer (batch) reactors; single wafer stagnation point flow reactors; single wafer rotating disk reactors; and, vapor levitation epitaxy reactors. Each of these reactor types will be discussed at length in the next several pages.
2. Literature Review

2.1.1. Batch reactors

A batch reactor, such as that shown in figure 2.1, is typically operated at process pressures on the order of 0.5-1 Torr and is thus classified as a Low Pressure CVD reactor. At these low pressures, the reactor geometry can take advantage of high gas diffusion rates which are

![Diagram of LPCVD reactor](image)

Figure 2.1. Schematic of LPCVD reactor: (a) overall system, and (b) wafer positioning.
typically three orders of magnitude greater than at atmospheric pressure. The chemical reactions occurring at the wafer surface are thus reaction rate limited rather than mass transfer limited. One of the potential problems with the LPCVD hot wall reactor, one in which the walls of the reactor are heated to prevent precursor condensation, is that deposition may occur on the reactor walls themselves. These deposits then flake off generating particles that may land on the substrate creating impurities within the film. These impurities usually prove to be devastating to electronic devices since they create discontinuities within the interconnects. However, periodic cleaning of the reactor at specified intervals can help to eliminate this condition.

As seen above, the wafers are placed within the reactor perpendicular to the flow of reactant gas. This particular reactor type is generally constructed with a quartz tube which allows external lamp banks or resistive heating to be employed for the purpose of wafer heating by thermal radiation and/or conduction. The flow in the annular region between the wafer edge and the inner surface of the tube is laminar and because the pressure is low, the high diffusion rates result in rapid radial mixing of the reactants between the wafers. These high diffusion rates are desirable since
the total effect of mixing caused by flow past the wafer edges is negligible.  

In this reactor, as in most LPCVD reactors, the pressure drop from the point of gas entry to exit is quite small and is ignored in mathematical modeling. The work presented by Jensen et al, goes to great lengths in deriving the mathematical expressions describing the process involving the deposition of polycrystalline silicon from SiH₄ gas (Silane) in this type of reactor. This particular process was chosen since there is an abundance of experimental data available from which to verify the model as well as its extreme importance in electronic devices.

A common practice in LPCVD processes is to dilute the process gas in some inert carrier gas such as N₂, Ar, or H₂. Here, the definition of an inert gas with respect to CVD processing is one which does not interfere with the growth of the desired film. For example, the dilution of silane gas with N₂ does not hamper the growth of pure silicon, whereas a carrier gas such as O₂ would. Additionally, some carrier gases act as catalysts in the reaction. An example of this type of process is that which this thesis is centered upon and will be discussed later. Nevertheless, the dilution process offers the advantages of reducing sensitivity to small flow disturbances and reducing the
temperature differences from wafer to wafer which are needed to obtain uniform film thickness. This temperature uniformity is also advantageous since it produces uniform grain sizes throughout the wafer resulting in more uniform electrical properties than could otherwise be obtained. There are, however, some disadvantages to diluted processing. One disadvantage is that pumping speeds must be greater to accommodate the increase in total gas flow, and another is that less of the reactant will reach the wafer requiring an increase in run time with a simultaneous decrease in overall system efficiency.8

Jensen states, "the ultimate goal in LPCVD [deposition] is to grow [films] with constant thickness and material properties."9 Due to this reactor geometry, it becomes necessary to either vary the temperature of the wafers along the reactor or dilute the constituents in order to achieve this goal. A continuously stirred tank reactor (CSTR) could also accomplish the ultimate goal, but these types of reactors are very expensive and have moving parts within the reactor which generate particles. The most attractive solution to the entire problem is to fit the system with a recycle loop as shown in figure 2.2. It has been shown that for the same pumping speed and reactant feed, the reactor outfitted with the recycle loop had a higher efficiency than
both conventional and conventional-diluted LPCVD processing. The end result of this observation is that reactor designs of the future should try to incorporate recycle loops if the process can withstand exposure to its own byproducts.

Figure 2.2. LPCVD reactor with recycle loop. (recycle ratio = $F_r/F_{ex}$)
2. Literature Review

2.1.2. Stagnation point flow reactors

Although the batch type reactors have a somewhat higher overall throughput, and therefore produce a given quantity of wafers which are less expensive, they do possess an inherent lack of reproducibility from wafer to wafer and especially from batch to batch. This problem is primarily due to depletion of the reactants as they pass through the reactor and lack of control of what occurs on each individual wafer. Each of these issues can be adequately addressed in a single wafer CVD reactor. Additionally, with the advent of new cluster tool formats, where each process module is isolated from the others as depicted in figure 2.3, a CVD reactor may be combined with several other process chambers to further enhance its overall throughput of finished product.

Due to its geometric simplicity, a single wafer stagnation point flow CVD reactor is an attractive candidate for mathematical modeling and analysis. These reactors are typically characterized by having the precursor delivery source parallel to a single substrate. However, to realize such a simple, yet powerful reactor in practice is more difficult than it may appear unless there is a thorough understanding of its design and operational constraints. A
few of the most important constraints in any reactor design are the reactant delivery system, overall system dimensions, modes of heat transfer, and method by which the substrate is attached to the heater itself. The last constraint is somewhat less important since in most Low Pressure CVD processes the overall heat transfer coefficient between the heater and the substrate is considerably higher than in most
other high vacuum processes operating at pressures 100 times lower.

The geometry of stagnation point flow CVD is such that a plane of reactant gas impinges the surface of the substrate as shown in figure 2.4 below. Since the gas is continuously supplied from the entire surface of the flow source, a uniform boundary layer of thickness $\delta_s$ is formed over the entire substrate. In this type of flow situation, the axial velocity becomes independent of its radial position along the substrate and can be considered a one dimensional flow field for the purpose of modeling. Additionally, factors such as chemical reactant concentration, temperature distribution, and other flow

![Figure 2.4. Schematic of fluid flow in stagnation point configuration; $\delta_s$ is the boundary layer thickness on the substrate.]
properties can be taken as constant. The net effect of these simplifications is that the partial differential equations describing the entire system reduce to simple differential equations yielding exact solutions to the Navier-Stokes equations.\textsuperscript{14}

The geometric properties of a typical stagnation point flow CVD reactor are the most critical aspects of the system as previously alluded to. Parameters such as flow source to substrate distance \((h)\), inlet diameter \((D)\), and the angle of divergence \((\theta)\), as shown in figure 2.5, can seriously impact the overall performance of the reactor. As the diagram indicates, the width of the hydrodynamic boundary layer \((\delta_w)\) depends on the vertical position relative to the reactor inlet. It also depends on gas constants such as its viscosity and velocity. This boundary layer region is inherently unsuitable for providing a planar source to the substrate thus indicating that the value of 'h' should be minimized as much as possible. Additionally, the thermal convection which results from the heater will serve to destabilize the flow profile. This configuration therefore lends itself to the establishment of counter-current flows (vortices) in the spacious regions above the substrate.
However, the advantage of such a configuration is the simplicity of its overall design as well as the relative ease of substrate loading and unloading from the reactor.

The alternative to the reactor configuration shown above is the inversion of the entire system as shown in figure 2.6. There are essentially two major advantages
associated with this configuration. The first is that thermal convection assists forced convection which helps to stabilize the flow in high pressure type processes. However, this effect is not as prevalent in systems designed for operation at lower pressures such as the one being studied in this thesis. The second is that since the wafer is mounted upside-down, the issue of particle contamination

Figure 2.6. Schematic of an inverted stagnation point flow CVD reactor.16
is significantly reduced. The only major disadvantages to this type of reactor configuration are the complexities, and their associated expense, of wafer loading/unloading and clamping of the wafer to the heater.

2.1.3. Rotating disc reactors, (RDR)

There are three flow geometries which can be represented in the limit of one-dimensional flow fields.\textsuperscript{17} The first, impinging jet flow, is a special case of stagnation point flow (which has already been discussed here). The second is channel flow which relies on a fully developed gas flow between two parallel plates or within a tube as shown pictorially in figure 2.7 below.

![Figure 2.7 Fully developed flow profile between two parallel plates or inside a tube.](image)

The third flow case is called rotating disc flow. This flow case can be visualized by a disc rotating about its central
axis with a stagnation flow imposed upon it as shown in figure 2.8. This particular flow case has at least three advantages and only two disadvantages. The first advantage is that the flow field in the vicinity of the substrate can be modeled as a one dimensional radial flow very similar to that of a stagnation point flow field. The only major

Figure 2.8 Flow field diagram for the rotating disc configuration where R is the substrate radius, r is the radial position, $\omega$ is the angular velocity, and $\phi$ is the angular position.\textsuperscript{18}
difference between the two cases is that in the RDR there is a net angular velocity of the reactants across the substrate. Another distinct advantage is the uniformity of the films produced. Since the substrate is rotating, any non-uniformities due to injector design or lack of reactor symmetry (including the heat and/or plasma sources since they generally do not rotate with the substrate) will be distributed, or smeared, across the face of the substrate at that particular radius as shown in figures 2.9a and 2.9b below. This fact enables the process engineer to pin-point the radial location of the problem area and take corrective action while still

Figure 2.9a,b. Examples of substrates with local and radial non-uniformity.
producing acceptable films. Finally, another advantage is the reduction of contaminants which are deposited onto the substrate. As previously stated, a downward flow CVD reactor is not the optimum configuration to employ from the standpoint of particle contamination. These particles simply fall and settle into the deposited film and create voids within semiconductor devices. However, it can be shown that through substrate rotation, these particles experience a centripetal acceleration which serves to accelerate the particle outward across the wafer surface with increasing radial speed. The net result is that the particle's momentum carries it beyond the edge of the substrate where it is subsequently pumped from the system.

There are, however, at least two drawbacks to this gain in reactor performance; complexity and price. As the complexity of a system increases (ie: more moving parts and more sophisticated control equipment), the corresponding price increases and the reliability generally decreases. In these cases, it becomes necessary for the semiconductor manufacturer to perform a cost/benefits analysis to determine whether or not the increased cost and decreased system reliability can be justified based upon throughput and/or yield requirements.
2.1.4. Vapor levitation epitaxy reactors, (VLE)

The vapor levitation epitaxy process is a relatively new thin film growth technique for semiconductor crystals and thin films. This deposition method is characterized by an upward flow of reactant gases against a "floating" circular semiconductor substrate.\textsuperscript{19} This is done by placing the substrate over a horizontal, porous frit through which the reactant gas stream flows as shown in figure 2.10 below.

![Diagram of vapor levitation epitaxy reactor](image)

Figure 2.10 Example of a "floating" substrate in a vapor levitation epitaxy reactor.\textsuperscript{19}
An inverted stagnation point flow distribution develops between the substrate and the frit (see figures 2.11 and 2.12 below) which simplifies the modeling of this reactor.

Figure 2.11 VLE reactant flow streamlines with a stagnation point in the center and a uniform exit velocity profile (not to scale).\textsuperscript{21}

Figure 2.12 Radial flow velocity profile.\textsuperscript{22}
Hydrodynamic modeling of this process has been achieved by application of the Navier-Stokes equations for two dimensional fluid flow. The end result, as reported by Osinski et al, is that this process can be represented by a few simple algebraic expressions for pressure, velocity, and levitation height as a function of gas viscosity, velocity, and substrate size and weight. Additionally, since the reactants emerge from the heated frit, they assist the heat transfer process between the substrate and the heater; a characteristic which makes this process unique.
2.2. Alternative Deposition Techniques

Chemical Vapor Deposition is an excellent method for producing high quality thin films for the semiconductor industry. However, there are at least two circumstances for which CVD processing may be less desirable. The first instance occurs when the CVD method proves to be much more costly than other more traditional deposition methods, such as Physical Vapor Deposition, Electron Cyclotron Resonance, and/or Rapid Thermal Processing. The other instance occurs when an adequate precursor carrier either has not or cannot be developed for the material of interest or is simply too difficult, or toxic, for companies to deal with. For example, deposition of Copper is accomplished using many

Figure 2.13a. Copper (I) Trimethylvinylsilane Hexafluoroacetylacetonate molecular structure.
2. Literature Review

different chemistries. The two chemistries used in this research have been Cu(II) hexafluoroacetylacetonate (hfac) and Cu(I)(trimethylvinylsilane)(hfac) as are shown in figures 2.13a & 2.13b. Both of these chemical precursors have been engineered such that their respective by-products are only mildly toxic and are somewhat easy to dispose of using a chemical "scrubber." Conversely, a process developed for the deposition of Tantalum produces Chlorine gas which is extremely toxic and more difficult to dispose of since it requires special equipment to filter it from the exhaust prior to atmosphericventing. For these reasons, and others, alternative deposition methods are used and will be discussed here briefly.
2.2.1. Physical vapor deposition, (PVD)

A. Sputtering

The process of Sputter deposition of thin films was discovered as early as 1877, but was not seriously employed until around 1930 when General Electric began sputtering thin films of gold for use as a base for subsequent plating. Throughout years since, many more applications for this technology have been developed. Essentially, sputtering involves the bombardment of a negatively charged target material with a positively charged, high energy ion (usually Argon ions) which physically "knock off" the target atoms. These free atoms from the target drift within the vacuum chamber until they adhere to another surface, preferably the substrate as shown below.

Figure 2.14. Schematic of a sputtering system.
This explanation of sputtering is admittedly quite over-simplified, but it sufficiently describes the essence of what is happening within the system. Sputter technology is still widely used by semiconductor equipment manufacturers because, even with its limitations as described in the introduction, it still possesses many advantages over other deposition methods. Some of the specifics associated with sputtering are:

1. Sputtering yields and corresponding deposition rates vary for different metals, alloys, and insulators. This is primarily due to the different molecular structures and bond strengths of the target material.

2. Films of complex materials can be sputtered by a process known as co-sputtering using multiple targets or by using an homogeneous target source produced for that purpose. For example, production of a Ni-Fe film requires the use of a high purity Ni-Fe target.

3. Film-thickness control is simple and easily reproduced. For the most part, the deposition rate is dependent upon deposition time and power for a given target material.
4. Sputtering with good uniformity generally requires the use of large area targets. The disadvantages to this are that the material must be available in sheet form and these sheets tend to be costly in their purest grade.

5. There are no difficulties associated with the material "spitting" as sometimes occurs in thermal evaporation.

6. There are no restrictions regarding gravitational forces in electrode or substrate arrangement (this is true of most vacuum processes).

7. The plasma can be manipulated to achieve greater film thickness uniformity (a major advantage). This manipulation is performed either mechanically (through appropriate use of shielding) or magnetically which will be discussed shortly.

8. High energy electrons can be kept away from the substrate preventing excessive substrate heating. This is performed through magnetic confinement of the plasma to regions distant from the substrate.

9. Negative biasing of the substrate can be used to improve the adherence, stress characteristics, and other film properties during the deposition of thin...
films. It can also be used to remove contamination from the surface of the film in a process known as etching. (Etching is essentially the reverse of sputtering. Here, material is actually sputtered from the substrate whereby removing contaminants from its surface before new film layers are added. This newly exposed surface then provides for an excellent adhesion layer for the next thin film to be deposited. It is worthy of stating that etching is a process common to nearly all forms of deposition, including CVD.)

10. Sputtering is capable of producing non-porous films with surfaces resembling the original substrate surface.

11. Until recently, the main disadvantage of sputtering was the relatively low deposition rate. Again, electromagnetic confinement of the high energy electrons and ions in the vicinity of the target surface has virtually eliminated this problem. For example, a traditional diode is capable of depositing roughly 2000Å/min where a high power planar magnetron is capable of deposition rates in excess of 10,000Å/min.
There are essentially two types of sputtering. The first is called Planar Diode Sputtering where the target assembly is given a negative electric charge using either Direct Current (DC) or Radio Frequency (RF) voltage thus establishing the cathode of an electric circuit. The vacuum chamber, substrate holder, and the substrate, which are either grounded or left positively charged with respect to the cathode, establish the anode. A "plasma," (consisting of electrons, neutrons, positively charged Argon ions, and neutral Argon atoms) is then established between the cathode and the anode after energizing the system as shown in figure 2.15a. This plasma provides the means through which electric current flows from the anode to the cathode. The positively charged Argon ions within this plasma are what is responsible for sputtering as they are strongly attracted to the negatively charged target. Essentially, they impinge on the target with sufficient force as to dislodge the target atoms which then travel to the surface of the substrate.

The second type of sputtering is nearly identical to the first except that a magnetic field is imposed on the face of the target cathode. The electric field, which is already present, and the magnetic field combine vectorially the net result of which is an increase in deposition rate
due to the dense confinement of the plasma in a region very close to the target as shown in figure 2.15b. Additionally, as previously stated, the high energy electrons located within the plasma region are confined to the target area. This prevents them from striking the substrate subsequently causing the substrate to heat up as the energy is transferred from the electron. The problem of substrate heating is a serious one since most semiconductor devices are incapable of withstanding high temperature environments and adequate heat transfer is difficult, at best, to provide in a vacuum environment.

B. Evaporation

The process of Evaporation is a relatively simple one. A material, usually a metal, is placed in a high vacuum environment and then melted. The molten material then
evaporates much as a puddle of water evaporates when the sun shines upon it. These evaporated atoms are then free to drift about throughout the evaporation chamber until they come into contact with and stick to another surface. It is, of course, desirable for the surface of adhesion to be the substrate which is to be coated.

There are several methods employed for melting the evaporant. One way is to place the material in a metallic crucible capable of withstanding high electrical currents. When this high current flows, the crucible gets extremely hot and melts the material to be evaporated. This method works very well and is inexpensive. However, problems occur when the material to be evaporated either has a higher melting temperature than the metallic crucible or when alloying or chemical reactions occur.

The development of the Electron Beam Gun eliminated the problem just presented. Essentially, the E-beam gun emits a high energy stream of electrons which are then magnetically guided toward the evaporant. This high energy beam strikes the evaporant which heats and melts the material from within the vacuum chamber. Since only the evaporant material itself heats up, the system can be water cooled and designed for longer life. Another advantage of this type of
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Evaporator is that the evaporant can be continuously fed to the system from the bottom as shown in figure 2.16.

![Figure 2.16. Schematic representation of a typical electron beam evaporation source.](image)

2.2.2. Electron cyclotron resonance, (ECR)

The ECR reactor presented in the literature was built for the deposition of Copper films by researchers at IBM's T.J. Watson Research Center. This reactor generated a low energy ionized copper plasma near the substrate without the use of buffers or carrier gases. This deposition process
has shown excellent via filling characteristics and has been successfully modeled.\textsuperscript{27}

The apparatus, shown in figure 2.17, is constructed such that microwave energy (2.45 GHz) enters the reactor through a quartz window. This energy is then transferred to a region where a high density, low energy plasma is created. The plasma is suspended in this region by a series of electromagnets. Deposition of the ionized Copper within the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2_17.png}
\caption{Schematic diagram of an ECR source. Note the series of magnets.\textsuperscript{28}}
\end{figure}
plasma is performed using another set of electromagnets which are responsible for transporting stream of this plasma toward the substrate region. At this point, the ionized copper ions experience a coulombic attraction to the biased substrate where they are deposited. (The source of copper atoms is an evaporation crucible as previously described.)

2.2.3. **Rapid thermal processing, (RTP)**

Rapid thermal processing is a deposition method in which the substrate is heated to extremely high temperatures (typically 800-1000°C) to cause a rapid change to occur on the surface of the substrate. For example, a common practice within the semiconductor industry is to coat a silicon substrate with an oxide film. This process is carried out by exposing the hot substrate to an oxygen rich environment thereby causing the surface of the substrate to oxidize. The oxide layer then provides corrosion protection and can also serve as a barrier layer between the silicon and films that would otherwise react with it.

The best understood and most commonly used applications of RTP technology are:

- Ion implant annealing
- Boron Phosphorous Silicate Glass (BPSG) reflow
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- Silicide formation
- Contact alloying
- Oxidation and Nitridation

Each of the applications listed above are crucial to the production of semiconductor devices. One of the greatest characteristics inherent to RTP technology is that it makes it possible to selectively enhance certain processes while simultaneously suppressing or eliminating others as summarized in table 2.1 below.

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>ENHANCE</th>
<th>SUPPRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Implant Anneal</td>
<td>Crystal Repair</td>
<td>Diffusion</td>
</tr>
<tr>
<td></td>
<td>Dopant Activation</td>
<td>Impurity Clustering</td>
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<tr>
<td>Glass Reflow</td>
<td>Topographical change</td>
<td>Autodoping</td>
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<tr>
<td></td>
<td></td>
<td>Junction Diffusion</td>
</tr>
<tr>
<td>Silicides</td>
<td>Phase Formation and Control</td>
<td>Side Reactions</td>
</tr>
<tr>
<td>Contact Alloying</td>
<td>Interface Reactions</td>
<td>Bulk Reactions</td>
</tr>
<tr>
<td>Oxidation/Nitridation</td>
<td>Real-Time Control of Film Growth Kinetics</td>
<td>Process Limited</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reactions</td>
</tr>
</tbody>
</table>

Table 2.1. Summary of RTP applications and process control.

All of the deposition methods presented in this review have specific applications for which they are best suited. Chemical Vapor Deposition, however, has proved to yield the best results for the deposition of copper thin films for use as interconnects and was therefore chosen as the deposition method for this research.
3.1. Overall System Design

The primary objective of this research is to design an effective CVD reactor capable of producing high quality copper thin films. The process of designing a CVD reactor is not necessarily a difficult task to undertake. However, designing a CVD reactor which produces consistently good films possessing the qualities valued by the semiconductor industry can take several months, or even years. For example, the reactor used for this research and development project took approximately six months to design and build. This process would have taken much longer had there not been a large knowledge base from which to draw ideas from.

Essentially, a CVD system can be divided into four major components: the controls assembly; the pumping assembly; the CVD reactor assembly; and, the CVD injector assembly, the latter two of which are shown in figure 3.1. All of these components must be made to work together if the system is to run properly.

3.1.1. Controls assembly

One of the first decisions to be made when designing any system is how one intends to control it. The main computer control system chosen here was a Techware Systems
Figure 3.1. Reactor and injector assemblies.
Cluster Module Controller (CLMC). This controller is ideally suited to this type of system as it is a step by step iterative controller with batch recipe processing capabilities. Additionally, it is specifically tailored to controlling analog input/output signals as well as discrete input/output signals. This controller may also be equipped with up to six RS-232 serial ports. Given the flexibility of the controller, the other system components could be chosen with little regard to control structure.

High vacuum pressure measurements ($10^{-2}-10^{-6}$ Torr) were performed using MKS Capacitance Manometers on both the substrate loadlock and the reactor. Rough vacuum pressure measurements were performed using CVC Products Thermistor gauges, again on the loadlock and reactor. An additional convectron gauge was placed on the pump-stack for safety purposes (if the pump failed, this gauge would trip safety interlocks and discontinue processing). The analog voltages corresponding to pressure were then fed back to Techware and converted to pressure readings using look-up tables which had been previously defined.

Radio Frequency (RF) power delivery and control was handled using an ENI ACG-3, 300 Watt power supply and an ENI MW-5 impedance matching network. All of these instruments were controlled by Techware using serial communications and
analog control signals respectively. The purpose of the RF power will be discussed later.

Gas delivery and control (Nitrogen, Hydrogen, and Argon) was performed with MKS model 2259B Mass Flow Controllers. Each of the MFCs were specifically calibrated for their respective gases and were also controlled using analog signals from Techware. The Liquid Delivery System (model LDS-100) and Liquid Vaporizer were also from MKS and were serially controlled through Techware.

The only other major sub-assembly controlled automatically through Techware was the Leybold turbo pump controller (model NT 150/360). Control of this system was performed by the opening and closing of a relay through Techware in order to turn the pump on and off.

Some system components were easier to control in manual mode and/or did not have provisions for automatic control. All heating of the gas injection feed tubes was handled with OMRON manually set temperature controllers in conjunction with an assortment of Omega heat tapes. The reactor pump-stack was also heated in this way. Another major sub-assembly, the West model 3800 PID substrate heater controller, was operated manually except for turning the power to the heater on and off through Techware. Finally,
the metering valves on the gas injector were controlled manually as a matter of preference and cost.

3.1.2. Pumping assembly

The next major assembly to address is that of pumping of the entire system. Pump selection is crucial to the process since the pump size is process dependent. For example, the process initially used in this thesis required a maximum flow rate of ~1000 SCCM of H₂ and ~500 SCCM of copper precursor. The process pressure is expected to be approximately 1 Torr. Therefore, any gas entering the process reactor will expand 760 times (as per the ideal gas law) and the 1500 SCCM would expand out to 1,140,000 CCM = 1140 L/min. This expanded gas is equivalent to ~41 cfm which, when combined with the system geometry and their resulting conductance, dictated a pump capable of 80 cfm. Additionally, this pump was selected with a 1.25 factor of safety to allow for any possible future changes in the process variables and gas flow rates. Therefore, an Ebara 80x25 rough dry pump was chosen with a front end Root's blower which proved capable of pumping the system to a base pressure of 5x10⁻⁴ Torr. The use of a dry pump, which is typical in CVD processing, was necessary to avoid the
possibility of backstreaming, a condition in which the pump oil diffuses back through the pumping system into the process chamber, thereby contaminating the reactor.

The pump is connected to the reactor and loadlock assemblies through 4" and 1½" stainless steel tubing respectively. A more uniformly high conductance pumping path would have been preferable, but was not possible due to cost and time constraints. The reactor can then be pumped directly by the roughing pump during the process by opening and closing the appropriate valves. The high conductance 4" tubing also has a Leybold 150 L/s turbo pump mounted to it to provide for base pressure pumping of the system to about 5x10⁻⁷ Torr. The base pressure condition must be met prior to running any deposition processes in order to achieve optimum film purity. As stated, the loadlock assembly is also pumped to about 1x10⁻³ Torr with the substrate inside (prior to placing the substrate into the reactor) by the roughing pump. This step helps to ensure the wafer has outgassed and reduces the exposure of the reactor to atmospheric contaminants.

The last major component of the pumping assembly, and perhaps the most important, is the Novapure Series 200 Effluent Gas Scrubber. The purpose of the scrubber is to remove any harmful byproducts of the reaction from the
exhaust gas prior to atmospheric venting. This component must be carefully chosen based upon the chemistry of the byproducts and the flow rates of the process gases. If either of these specifications are incorrect, serious injury to personnel and/or the environment is possible. Additional protection is also provided by the dilution of the effluent and by the use of an eight foot tall exhaust stack on the roof of the building.

Finally, the exhaust suitable for atmospheric venting had to be routed to the roof through 8" ducting which was headed by an 500 cfm explosion-proof blower. This blower had to be explosion-proof since the exhaust gas from this particular process contains Hydrogen which can be explosive.
3.1.3. CVD reactor assembly

The reactor assembly essentially consists of the reactor chamber and the substrate heater assembly as shown below. This particular reactor started its service life as an RTP chamber and as such already had a nicely finished, corrosion resistant, stainless steel body with built in oil channels in the chamber walls and base for the purpose of chamber heating. Additionally, since RTP processes are also dependent on laminar fluid flow, the chamber was circular and quite symmetric internally (symmetry is very important

Figure 3.2. CVD reactor and heater assembly.
in any flow dependent process). The only assemblies required to convert this chamber into a CVD reactor was a precursor injection source and a substrate heater.

The substrate heater, as shown in figure 3.3, was adapted from an older design used by CVC Products for a different application. However, the technology employed in its construction was found to be quite reliable, relatively easy to manufacture, and suitable for CVD applications.

The heater consists of an Inconel block 7" in diameter with a milled channel into which a coaxial heating element (purchased from Philips Thermocoax) is permanently brazed. This heater assembly is capable of reaching temperatures in excess of 800°C (although here it will only need to reach a
maximum of \( \sim 250^\circ C \). Additionally, a thermocouple is mounted on the back side of the heater which allows for closed loop control of the heater temperature using the West 3800 PID controller.

Finally, this reactor will soon possess the capability of variable injector source to substrate spacing using a substrate/heater lift assembly. After the substrate is placed on its palette carrier, it is pumped down in the loadlock. The substrate and palette are then transferred into the reactor at a height of 1100 mm from the floor (this is an industry standard). Once inside, the substrate will then be moved up or down from this position using a linear actuator (which is controlled through Techware) as shown in figure 3.4. This capability will also allow for the use of injector plates of varying thicknesses, a subject which will be discussed later.
Figure 3.4. Substrate heater/lift assembly.
3.1.4. CVD injector assembly

The final major component of this CVD system is the precursor injector assembly which, given a properly designed and controlled reactor, is the most important assembly on the entire system. This assembly's sole responsibility is to delivery the process reactants in such a way as to maximize all film properties of interest. As such, a great deal of time and effort goes into its design and is what the majority of this research is centered upon.

In the case of liquid chemicals, such as those used here, a precursor ampule, liquid pump, and vaporizer must be employed. The precursor ampule is pressurized to 20-25 psi which is sufficient to push the liquid chemical to the injector pump. This pump, the LDS-100 purchased from MKS Instruments, then takes the liquid and pressurizes it to ~300 psi and also meters the output flow to the vaporizer. The high pressure liquid then enters the vaporizer and is forced through a series of very thin (~.001" thick), tightly packed, heated, stainless steel disks. There can be anywhere from 10 to 100 disks inside the vaporizer depending upon the vaporization characteristics of the liquid. While being forced through these disks, the liquid turns into a dense vapor. This chemical vapor is then mixed with a
carrier gas, either Hydrogen or Nitrogen for this research, at which time it flows toward the injector through a large diameter tube, as shown schematically in figure 3.5 below.

![Liquid Delivery System Diagram](image)

Figure 3.5. Precursor delivery schematic.

Upon reaching the injector assembly the gas passes through one of four metering valves. These valves are used to govern the amount of gas delivered by each of the four zones of the injector. The metered gases then travel into a series of concentric, relatively isobaric, regions on the back side of the injector plate. The injector plate has
several holes drilled into it which are coincident with each of the four regions (see figure 3.6). The number of holes in each zone and their diameters are determined based upon the desired flow characteristics of the process (ie. flow rates and gas composition) and will be discussed at length in the next section.

Another important factor in the design of the injector assembly is that all components must be capable of high temperature operation. This requirement stems from the fact that the vaporization process in the vaporizer relies upon
heating the vapor/carrier gas mixture beyond its vaporization temperature. If the gas comes into contact with a cool surface after vaporization, it will condense on that surface and destroy the process. In the cases of Cu(I) and Cu(II) chemistries, it is necessary to keep the vaporizer/injector assemblies, including all tubing and valving, at ~60°C and ~105°C respectively. Additionally, the valves must also be capable of being exposed to an internally corrosive environment.
3.2. CVD Injector Design

The heart of a CVD reactor lies not in how it is controlled or pumped, but in how well it delivers the reactants to the substrate. If the reactor falls short of this goal, it is worth little more than its weight in scrap metal! Therefore, it is necessary to pay considerable attention to the design of each specific part of the injector as it will ultimately determine the quality of the films it produces. However, as with all things in life, designs continue to get better as the designer's experience base and education level continue to grow; as is the case with the injector designs to be presented here.

This section will first open with a brief introduction to Stagnation Point Flow theory (which governs this reactor/injector combination) followed by mathematical modeling of the injector based upon the equations which result from that theory. The model will then be used to analyze variations of the injector plate design reflecting improvements which have been made to the system.

3.2.1. Stagnation point flow theory

The basic description of a stagnation point flow CVD reactor has already been covered in section 2.2.1. However,
3. CVD Reactor/System Design

the fundamentals of stagnation point flow theory have not yet been covered and seem to be an appropriate starting point. Stagnation point flow in a CVD reactor is a mass transport process governed by the Navier-Stokes equations for constant gas density and viscosity. The equations, in cylindrical coordinates, are:

\[ \rho \left( \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_{\theta}}{r} \frac{\partial v_r}{\partial \theta} + \frac{v_z}{r} \frac{\partial v_r}{\partial z} \right) = \rho g_r - \frac{\partial p}{\partial r} \\
+ \mu \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r v_r \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_r}{\partial r} + \frac{\partial^2 v_r}{\partial z^2} \right\} \]  

\[ \text{r-component:} \]

\[ \rho \left( \frac{\partial v_{\theta}}{\partial t} + v_r \frac{\partial v_{\theta}}{\partial r} + \frac{v_{\theta}}{r} \frac{\partial v_{\theta}}{\partial \theta} + v_z \frac{\partial v_{\theta}}{\partial z} + \frac{v_z}{r} \frac{\partial v_{\theta}}{\partial \theta} \right) = \rho g_{\theta} - \frac{\partial p}{\partial \theta} \\
+ \mu \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r v_{\theta} \right) + \frac{1}{r^2} \frac{\partial^2 v_{\theta}}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_{\theta}}{\partial r} + \frac{\partial^2 v_{\theta}}{\partial z^2} \right\} \]  

\[ \text{\theta-component:} \]

\[ \rho \left( \frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_{\theta}}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \right) = \rho g_z - \frac{\partial p}{\partial z} \\
+ \mu \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r v_z \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2} \right\} \]  

\[ \text{z-component:} \]

These equations can be expressed much more compactly in vector form as follows:

\[ \rho \frac{\partial \vec{v}}{\partial t} = \rho \vec{g} - \nabla p + \mu \nabla^2 \vec{v} \]  

\[ \text{(3.2)} \]

The constant properties assumption is valid for the case of gas flow analysis within the reactor chamber and inside isolated cavities of the precursor injector.
Difficulties arise when considering the expansion of the complex gas as it passes from one region within the injector assembly to another. For example, as the gas passes through the metering valves controlling each zone, there is not only an unknown pressure drop across the valve, but also a corresponding expansion of the gas due to the pressure drop as dictated by its equation of state:

\[ P = nkT \]  

(3.3)

where \( P \) is the pressure (Pa), \( n \) is the molecular density of the gas (molecules/unit volume), \( k \) is Boltzmann's constant \( (1.38 \times 10^{-23} \text{ J/K}) \), and \( T \) is the absolute temperature of the gas in Kelvin. Recall that the temperature of the gas does not change since it is held constant throughout the entire injector assembly as previously described. This being the case, not much attention was given to the analysis of the flow in these areas and more attention was given to the modeling and design of the injector plate itself.

After leaving the injector plate, the gas expands adiabatically into the reactor chamber. From this point forward, stagnation point flow exists between the injector and the substrate heater assembly. Given the constant
properties of the gas and the flow geometry of the reactor
chamber, the Navier-Stokes equations reduce to:

r-component:
\[ \rho \left( v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} \right) = -\frac{\partial P}{\partial r} + \mu \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial v_r}{\partial r} \right] \right\} \]  \hspace{1cm} (3.4a)

z-component:
\[ \rho \left( v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} \right) = -\frac{\partial P}{\partial z} + \mu \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial v_z}{\partial r} \right] \right\} \]  \hspace{1cm} (3.4b)

Note that the \( \theta \) component has vanished. This is due to the
fact that the reactor is assumed to be radially symmetric
through any cross section. This is a valid assumption
except for the region where the substrate enters and leaves
the reactor. However, this entry/exit plane lies below the
substrate surface when the heater/lift assembly is in the
raised position as shown in figure 3.7.

Finally, the last equation necessary for a full
analysis of the system is that which is concerned with the
conservation of mass. Basically, the continuity equation
states that whatever mass goes into the system, must come
out of the system as follows: \(^{31}\)

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( rv_r \right) + \frac{1}{r} \frac{\partial}{\partial \theta} \left( \rho \nu_0 \right) + \frac{\partial}{\partial z} \left( \rho v_z \right) = 0 \]  \hspace{1cm} (3.5)
The equations given thus far represent the conservation of momentum and total mass while the equation of state allows prediction of the behavior of the complex gas under various environmental conditions. The solutions to the reduced Navier-Stokes equations \((3.4a \& 3.4b)\) and the continuity equation yield the velocity components within the reactor \((v_r, v_z)\) and the local pressure at any point within the reactor. The pressure is obtained by knowing both the density (directly from equation 3.5) and the temperature of the gas at a specific point within the reactor and then using the equation of state to solve for the pressure. Upon
performing this calculation, one finds that the flow profile within the reactor will trace out streamlines similar to those shown in figure 2.4.

An alternative method to the approximation of the flow field existing between the injector source and the substrate surface is the use of superposition of ideal flows. The ideal flow appropriate to this flow case is the source flow which is represented by the complex velocity potential:

\[ \Omega = -\mu \ln(z - z_1) \] (3.6)

Recall that the value for \( z \) in the complex plane can be represented as follows:

\[
\begin{align*}
z &= re^{i\theta} \\
z &= r\cos \theta + i(r\sin \theta) \\
z &= x + iy
\end{align*}
\]

For a singularity located at \( z_1 \), the directed distance from that singularity to any point within the flow field is \( z - z_1 \) as shown above.\(^{35}\)

Now, utilizing the method of images, another source can be placed at a mirrored location across the x-axis from the
point $z_1$. The complex velocity potential representing this mirrored point is:

$$\Omega = -\mu_s \ln(z+z_1)$$  \hspace{1cm} (3.7)

Now, equations 3.6 and 3.7 can be combined utilizing the principal of superposition which states that any combination of ideal flows may be combined to yield another ideal flow case. Thus, the following expression is obtained by combining the two complex velocity potentials:

$$\Omega = -\mu_s \ln(z-z_1) - \mu_s \ln(z+z_1)$$  \hspace{1cm} (3.8)

Figure 3.8. Resulting flow field from the superposition of source and image flow.
Note how the net velocity profile is strictly vertical along a line connecting the real and image sources and also how the net vertical velocity is zero across the x-axis. This indicates that this flow case represents a source flow from the real source (+y) against a flat, circular plate. The source strength, $\mu_s$, is defined to be $q/2\pi$, where $q$ is the volume flow rate per unit depth. Additionally, it can be shown that the radial and angular velocities are:

$$v_r = \frac{\mu_s}{r} = \frac{q}{2\pi r} \quad \text{and} \quad v_\theta = 0 \quad (3.9a \ & \ 3.9b)$$

Now, the situation described above may be extended to this application by simply placing several source-image pairs at the appropriate locations as dictated by the injector plate design. Once accomplished, the resulting system of equations can be solved and the generalized flow field may be seen. The only problem with this simplified modeling approach is that additional flow cases may need to be added to the system to accommodate various boundary conditions within the reactor (ie. reactor walls). However, as previously mentioned, the superposition of source flows is sufficient to gain an adequate understanding of what is happening between the injector and the substrate.
The method of superposition is a very simplified approach to flow field analysis but does, however, have its limitations. For example, it is only valid for inviscid, incompressible flows and as such may not be suitable for some CVD analyses. More specifically, complications arise when dealing with viscous flows in a thermal CVD reactor. One must be aware of whether or not the flow will be dominated by thermal convection (due to the heater) or forced convection (due to the injector). The determination between the two is made using the ratio of the Grashof number to the Reynolds number squared, commonly known as the mixed convection parameter.

The Grashof number is a measure of the strength of natural convection in the system and is defined as follows:

\[ Gr = \frac{g^3 \beta \Delta T h^3}{\nu^2} \]  

(3.10)

where \( g \) is the acceleration due to gravity, \( \beta \) is the expansion coefficient of the gas which is defined as:

\[ \beta = \frac{1}{T} \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p = \frac{1}{T} \quad \text{for an ideal gas} \]  

(3.10a)
h is the separation between the injector and the substrate, and \( v \) is the kinematic viscosity of the gas. Note that the Grashof number is linear with the temperature difference between the gas entry temperature and the temperature of the heater and varies as the distance between these two points cubed. Since the Grashof number is to be minimized, the separation between the injector and the heater should be kept as small as possible, but large enough to sustain a stable flow field. Generally, buoyancy driven flows are likely to occur if this number is relatively large.\(^{37,38}\)

The Reynolds number, conversely, is a measure of the forced nature of the gas flow and is defined as:

\[
Re = \frac{D^2 \cdot v \cdot D}{\mu} = \frac{v^2 D}{v}
\]

(3.11)

where \( v \) is the gas velocity within the reactor and \( D \) is the inlet diameter. A large Reynolds number dictates a more turbulent flow whereas a small Reynolds number (below 2300) dictates a more laminar flow. For most low pressure, low flow processes, the Reynolds number is seldom higher than 100.\(^{37,38}\)

For the CVD reactor studied, hydrogen was initially used as the carrier gas and was present by a factor of at least 2:1 compared to any of the other complex gas
constituents. Therefore, its properties were used to determine the approximate nature of the flow within the reactor. The following table lists all of the information on the gas and the reactor pertinent to this calculation:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acceleration due to gravity</td>
<td>9.8 m/s²</td>
</tr>
<tr>
<td>Gas exp. coeff. (assumed ideal)²⁵</td>
<td>0.0024 K⁻¹</td>
</tr>
<tr>
<td>Nominal temperature difference (Injector=100°C, Heater=200°C)</td>
<td>100°C = 100 K</td>
</tr>
<tr>
<td>Nominal separation distance</td>
<td>0.025 m</td>
</tr>
<tr>
<td>Kinematic viscosity (@ 150°C)</td>
<td>2x10⁻⁴ m²/s</td>
</tr>
<tr>
<td>Gas velocity (inside rctr @ 750 SCCM flow)</td>
<td>0.32 m/s</td>
</tr>
<tr>
<td>Injector diameter</td>
<td>0.2 m</td>
</tr>
</tbody>
</table>

Table 3.1. Nominal values for reactor characterization.

Given these values, Gr=918.75 and Re=320. This yields a ratio of Gr/(Re)²=0.009. This value gives a clear indication that forced flow is dominant inside the reactor for this set of conditions. If the ratio were greater than unity, then thermal convection would dominate and create an unstable, perhaps turbulent, flow situation resulting in the degradation of reactor performance. Such a situation can occur if the flow rate is significantly reduced or the temperature difference between the injector and substrate heater is increased.
3.2.2. Modeling and system analysis

When this work first began, there were time constraints which had to be met and it was necessary to get the reactor designed and assembled as quickly as possible. Needless to say, nothing on the system was modeled prior to its initial assembly (except for obvious calculations such as pumping capacity). Therefore, after the system assembly was completed and all of the equipment ran properly, the process of modeling and improving the initial design could begin.

Having prior experience in CVD reactor design within CVC Products and being familiar with the reactor designs of its competitors, it was known that the reactor chamber to be used for this research would perform adequately. It was therefore not necessary to pay much attention to modeling or trying to optimize its performance. Similarly, since the liquid precursor pump and vaporizer assemblies were purchased, it was not necessary to model or optimize them. However, it was known that the most crucial element of the reactor was the design and optimization of the precursor injector assembly and that it would ultimately determine how well the reactor would perform. Therefore, most of the mathematical modeling was concentrated on this area.
3.2.2.1. Complex gas properties

Unfortunately, the gases being dealt with were not pure Hydrogen, Nitrogen, or some other combination of well documented/understood gases. This process used a mixture of Isopropyl Alcohol and bis Cu(II) hexafluoroacetyleacetonate (hfac) with Hydrogen as the carrier gas or Cu(I) trimethylvinylsilane (tmvs) hfac with Hydrogen or Nitrogen as the carrier gas. There is no data in existence, or at least none available from the chemical manufacturers, on the physical properties of the Cu(I) or Cu(II) precursors in the gaseous phase. This meant that data on density and viscosity had to be empirically derived or experimentally determined; within the limited scope of this investigation, the empirical approach was chosen.

The gas density and viscosity within the injector are required for characterizing the flow within the injector feed tube and across the injector plate (ie. laminar or turbulent). More specifically, they are used in the calculation of the Reynolds number. The Reynolds number is also used to determine the entrance length for the flow within the injector plate holes as well as frictional losses producing the pressure drop across the plate.
3. CVD Reactor/System Design

3.2.2.2. CVD injector model

The CVD precursor injector was modeled mostly through the use of incompressible flow theory. This approach is valid provided the analysis is restricted to regions within the injector which are relatively isobaric (ie. small pressure drops through the tubes). These regions include the flow through the main injector feed tube and the flow through the holes in the injector plate.

The software chosen for the modeling was Mathcad versions 4.0 and 5.0 PLUS (upgraded during the course of this research). This software was specifically designed for easy integration of mathematical formulae and text. It also provides a "live" interface enabling the modeler to view the effects of a change made to the system immediately upon its implementation.

The next few pages will describe step by step exactly what calculations the Mathcad document performs, in the order in which they are performed. The theory behind each of the computations will also be presented as appropriate, followed by an actual sample of the document on page 78 for review. The sample model given is that for the injector plate which has successfully produced copper films for over six months, the details of which will be discussed later.
3. CVD Reactor/System Design

a. Flow Rates: This opening section is where the user enters each of the constituent flow rates as established by the process requirements. The flow rate of Hydrogen is entered in standard cubic centimeters per minute (SCCM), the flow of Propanol is entered in millilitres per minute, and the flow of bis Cu(II) hfac is entered in grams per minute.

b. Conversions to Molar and Gas Flow Rates: The object of this section is to obtain the molar and volumetric flow rates of each of the complex gas constituents for later use. In the case of Hydrogen, it simply converts the user defined volumetric flow rate into the equivalent mass and molar flow rates, the computations for which are well understood utilizing the following equations:

\[ MFR = \frac{Q}{22400} \cdot MW \]  
(3.12)

where MFR is the mass flow rate in g/min, Q is the gas flow rate, 22,400 is a conversion factor with units of cm³/mol, and MW is the molecular weight in g/mol.

\[ mFR = \frac{MFR}{MW} \]  
(3.13)

where mFR is the molar flow rate in mol/min. The isopropyl alcohol's volumetric flow rate is first converted to a mass flow rate using the following:
\[ MFR = \rho \cdot \Gamma \quad (3.14) \]

where \( \rho \) is the density in g/cm\(^3\), and \( \Gamma \) is the liquid flow rate. The molar flow rate is then computed as before. Finally, using a modified form of the equation of state for an ideal gas, shown below, the molar flow rate is converted to a volumetric flow rate, where \( Q \) is the volumetric flow rate in SCCM, \( mFR \) is the molar flow rate in mol/min, \( R \) is the gas constant which has the value 8.314 J/mol*K, \( T \) is the standard temperature (273K), \( P \) is standard atmospheric pressure (1.013x10\(^5\) Pa), and the factor of 10\(^6\) is provided for conversion from m\(^3\) to cm\(^3\). Finally, the Cu(II) mass flow rate is converted to its molar flow rate and then, using the ideal gas equation of state, converted to its equivalent volumetric flow rate.

c. **Flow Summary:** The flow summary is simply provided for the convenience of the process engineer or analyst.

d. **Partial Pressures:** It is sometimes useful to provide the process engineer with partial pressure data to assist in process development. It will also be used to determine the densities of each of the constituents
within the injector in the following section. First the user enters the pressure expected on the back side of the injector plate (this is usually 1-5 Torr above the pressure of the reactor). Then, the pressure of the reactor (ie. process pressure) is defined. Using this information, the molar flow rates of each of the constituents, and the total molar flow rate, the document calculates the partial pressures of each "gas" inside both the injector and the reactor using the following equation:

\[
P_i = \left( \frac{m_{FR_i}}{m_{FR_T}} \right) \cdot P_x \tag{3.16}
\]

where \( P_i \) is the calculated partial pressure of the constituent (Torr), \( m_{FR_i} \) is the molar flow rate of the constituent (mol/min), \( m_{FR_T} \) is the total molar flow rate (mol/min), and \( P_x \) denotes the user defined pressure within either the injector or reactor chamber (Torr).

e. **Gas Densities:** The overall density of the complex gas will be required for future calculation of expressions such as the Reynolds number for flow characterization. Here, each of the partial densities are determined based upon their respective partial pressures within the injector using a modified form of the equation of state.
After each of the (partial) gas densities have been determined, they are simply added together since they all occupy the same space within the injector.

f. Complex Gas Viscosity: This section is perhaps the least understood for polyatomic gas molecules. There are several theories which have been proposed for calculating the viscosity of such a "gas", but none hold for all cases and all are approximate. The best way to determine the actual viscosity of such a gas is to experimentally measure it. In the absence of this capability, however, it can be approximated by knowing both the mass and molecular diameter of the molecule. In step 1 of this section, the user defines these values for use in the equations that follow. Then, the next step calculates the viscosity of each of the individual constituents based upon their temperature using the following equation:

\[ \mu = \frac{2}{3\pi} \cdot \left( \frac{1}{d} \right)^2 \cdot \left( \frac{mRT}{\pi} \right)^{\frac{5}{2}} \]  

(3.17)

where \( \mu \) is the viscosity (N·s/m²), \( d \) is the molecular diameter (m), \( m \) is the mass of the molecule (kg), \( k \) is Boltzmann's constant (1.38x10⁻²³ J/K), and \( T \) is the gas
temperature (K). Finally, the complex viscosity of the gas is found using formulae established by Wilkes.\textsuperscript{42}

\[
\phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-5} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{5}{25}} \left(\frac{M_i}{M_j}\right)^{\frac{25}{25}}\right]^2
\]  

(3.18)

\[
x_i = \frac{m_{FR_i}}{m_{FR_T}}
\]  

(3.19)

and,

\[
\mu_T = \frac{\sum_i x_i \mu_i}{\sum_i x_i \phi_{ij}}
\]  

(3.20)

where \(\phi_{ij}\) is a dummy variable, \(M\) is the mass of each molecule, \(\mu\) is the viscosity of each constituent, \(x_i\) represents the molar fraction of each constituent of the complex gas, and \(\mu_T\) is the complex viscosity.

g. **Injector Tube Characterization:** The characterization of the flow inside the injector tube is provided for the purpose of giving the process engineer some idea of what is happening to the gas as it passes through this portion of the system. First, it calculates the gas expansion coefficient based upon the changes experienced by the gas in both temperature and pressure as it passes from the vaporizer into the tube using another modified version of the ideal gas law as follows:\textsuperscript{43}

\[
\delta = \left(\frac{T_{inj}}{273}\right) \cdot \left(\frac{760}{P_{inj}}\right)
\]  

(3.21)
where $\delta$ is the gas expansion coefficient, $T_{inj}$ is the injector temperature (K), and $P_{inj}$ is the pressure inside the injector (Torr). The factors of 273K and 760 Torr are standard temperature and pressure respectively. The new volumetric flow rate of the "expanded" gas is also provided and used for calculation of flow velocities. Finally, the Reynolds number is calculated for flow characterization using the following relation:

$$ Re = \frac{\rho V D}{\mu} $$

(3.22)

where $Re$ is the Reynolds number (unitless), $\rho$ is the density, $V$ is the gas velocity inside the injector tube (m/s), $D$ is the injector tube diameter (m), and $\mu$ is the complex gas viscosity (N*s/m²).

h. **Injector Plate Characterization:** This is the most important section of the entire document and all of the previous calculations were performed to support it with the appropriate data. The user first enters the hole data pertaining to the injector plate to be modeled. Based upon this data, the document calculates the net gas flow velocity within each of the holes as follows:

$$ V = \frac{Q}{a} $$

(3.23)
where \( V \) is the gas velocity, \( Q \) is the complex gas volumetric flow rate (m\(^3\)/s), and \( a \) is the total area of the injector holes (m\(^2\)). The corresponding Reynolds number is also calculated for flow characterization. The next section calculates the total head loss by analyzing the major and minor head losses within each hole using the following equations:

\[
\begin{align*}
\h_L &= \left( \frac{64}{\text{Re}} \right) \cdot \left( \frac{L_{\text{hole}} - 0.5L_{\text{hole}}}{d_{\text{hole}}} \right) \cdot \left( \frac{V_{\text{hole}}^2}{2} \right) \\
\h_{Lm} &= K \cdot \left( \frac{V_{\text{hole}}^2}{2} \right)
\end{align*}
\]  

(3.24)  

(3.25)

where \( h_L \) represents the major head losses in the hole due to frictional effects (m\(^2\)/s\(^2\)), \( \text{Re} \) is the Reynolds number, \( L_{\text{hole}} \) is the length of the hole (m), and \( V \) is the complex gas velocity through the hole (m/s). In equation 3.25, \( h_{Lm} \) represents the minor head losses due to hole geometry (m\(^2\)/s\(^2\)), \( K \) is the loss coefficient for a given geometry, and \( V \) is again the gas velocity. Notice the approximation used in the calculation of the major head loss. The equation used pertains to fully developed, laminar flow in tubes where \( L_{\text{hole}} \) would define the length of the tube being analyzed. However, the entrance length cannot be ignored as it may extend a considerable distance into each hole and the head loss will be lower
for this distance. Therefore, the assumption was made that the head loss due to frictional flow would be zero at the hole entrance and steadily increase until it reaches the point where the flow is fully developed. Then, using a linear approximation for the increase in frictional effects, the total entrance length may be replaced by one half the entrance length. As such, the length of the injector holes to be used in calculating major head losses becomes \((L_{\text{ho1e}} - L_{\text{ent}}) + 0.5(L_{\text{ent}})\) which is equivalent to \((L_{\text{ho1e}} - 0.5 L_{\text{ent}})\). Finally, the information obtained is inserted into the energy equation (already reduced by cancellation) where the pressure drop across the injector plate is obtained.

i. **Injector Plate Characterization (cont.):** This continuation of the previous section is provided to discuss the final calculation of pressure drops for comparison. The first pressure drop, identified as \(\Delta P_{\text{plate}}\), represents the pressure drop calculated across the plate using the calculated head losses as follows:

\[
\Delta P_{\text{plate}} = \rho \cdot h_{L1} \cdot \left( \frac{760}{1.013 \times 10^5} \right)
\]

where \(\rho\) is the gas density \((\text{kg/m}^3)\), \(h_{L1}\) is the total head loss (equal to the addition of the major and minor head
losses), and the trailing ratio is used for converting from Pascals to Torr. However, this pressure drop is a function of the user defined injector pressure, \( P_{\text{inj}} \), from the Partial Pressure section. This injector pressure is then used to calculate the gas densities, expansion coefficient, expanded volumetric flow rate, and resulting flow velocities - all of which are needed to find \( \Delta P_{\text{plate}} \). The second pressure drop is the difference between the injector pressure, \( P_{\text{inj}} \), and the reactor pressure, \( P_{\text{rctr}} \), as defined by the user. Now, the only way that \( \Delta P_{\text{plate}} \) and \( (P_{\text{inj}}-P_{\text{rctr}}) \) can be equal is if the user supplied injector pressure satisfies both derivations of the pressure difference across the injector plate. This task is accomplished through an iterative process where \( P_{\text{inj}} \), defined by the user in the Partial Pressure section, is updated until both expressions are roughly equivalent and in the 1-5 Torr range: \( \Delta P_{\text{plate}} \sim (P_{\text{inj}}-P_{\text{rctr}}) \).

j. **Temperature Effects of Adiabatic Free Expansion:** The final section of this document calculates the drop in temperature experienced by the gas as it emerges from the injector plate and expands into the chamber. The
calculations for this process rely heavily on the pressure drop across the injector plate calculated in the previous section. The equation, shown below,

\[
T_{\text{rct}} = T_{\text{inj}} \cdot \left( \frac{P_{\text{rct}}}{P_{\text{inj}}} \right)^{\frac{y}{T}}
\]

is appropriately derived from compressible flow theory where \(T_{\text{rct}}\) is the temperature of the gas as it expands into the reactor (K), \(T_{\text{inj}}\) is the injector temperature (K), \(P_{\text{rct}}\) and \(P_{\text{inj}}\) are the reactor and injector pressures respectively (Torr), and \(\gamma\) represents the ratio of the specific heats of the gases at constant pressure and volume (\(C_p/C_v\)). The final temperature of each complex gas constituent gas is then provided for user interpretation. The importance of this calculation lies in the vaporization temperature of each constituent. For example, the vaporization temperature of isopropyl alcohol is 82.4°C, which corresponds to 355.4K, at standard temperature and pressure conditions. Therefore, if its temperature falls below this point, the alcohol will condense back into its liquid form. This effect is, of course, pressure dependent and can be examined using vapor pressure curves for those complex gas constituents for which one has been established.
CVC Products, Inc. Copper CVD Research Tool
Injector Manifold Flow Analysis

Researchers: Tom Omstead, PhD, Vera Versteeg, Tom Gebo, and Alan Stephens
Analysis by: Alan Stephens

This analytical document is for use in analyzing the flow characteristics of Hydrogen, Propanol, and bis (1,1,1,5,5,5, hexafluoroacetone)-copper(II), Cu(II)hfac precursor through the injection manifold for specified flow rates, temperature, and chamber pressure.

Flow Rates:

Hydrogen: \( Q_{h2} = 700 \) (SCCM - gas)

Propanol: \( \Gamma_{ipa} = 1.0 \) (ml/min - liquid)

bis Cu(II) hfac: \( \Lambda_{Cu} = 0.1 \) (g/min - solid)

Conversions to Molar and Gas Flow Rates:

Hydrogen:
1) Mass Flow Rate (MFR):
\[\text{MFR}_{h2} = \frac{Q_{h2}}{\text{MW}_{h2}}\]
\[Q_{h2} = 0.063 \text{ (g/min)}\]

2) Molar Flow Rate (mFR):
\[\text{mFR}_{h2} = \frac{\text{MFR}_{h2}}{\text{MW}_{h2}}\]
\[\text{mFR}_{h2} = 0.031 \text{ (mol/min)}\]

Propanol:
1) Mass Flow Rate (MFR):
\[\rho_{ipa} = 0.8035 \text{ (g/cm}^3\text{)}\]
\[\text{MFR}_{ipa} = \rho_{ipa} \Gamma_{ipa}\]
\[\text{MFR}_{ipa} = 0.803 \text{ (g/min)}\]

2) Molar Flow Rate (mFR):
\[\text{MFR}_{ipa} = \frac{\text{MFR}_{ipa}}{\text{MW}_{ipa}}\]
\[\text{mFR}_{ipa} = 0.013 \text{ (mol/min)}\]

3) Convert mFR to gaseous flow rate - Q
\[P^*(Q_{ipa}) = (mFR)^*(R^*T)\]

(Values for STP)
\[T_{std} = 273 \text{ (K)}\]
\[R = 8.314 \text{ (J/mol}^*\text{K)}\]
\[P_{std} = 1.01310^5 \text{ (Pa)}\]
\[Q_{ipa} = \frac{(\text{mFR}_{ipa}R/T_{std})}{P_{std}} \approx 300.053 \text{ (SCCM)}\]

Figure 3.9a. Injector flow analysis - page 1.
bis Cu(II) hfac

1) Mass Flow Rate (MFR):

\[ \text{MFR}_{\text{Cu}} := \lambda_{\text{Cu}} \text{ (g/min)} \]

\[ \text{MFR}_{\text{Cu}} = 0.1 \text{ (g/min)} \]

2) Molar Flow Rate (mFR):

\[ \text{MW}_{\text{Cu}} := 478.6 \text{ (g/mol)} \]

\[ \text{mFR}_{\text{Cu}} := \frac{\text{MFR}_{\text{Cu}}}{\text{MW}_{\text{Cu}}} \]

\[ \text{mFR}_{\text{Cu}} = 2.089 \times 10^{-4} \text{ (mol/min)} \]

3) Convert mFR to gaseous flow rate - Q

\[ P^*(Q\text{Cu}) = (mFR)^*(R^*T) \]

(Values for STP)

\[ T_{\text{std}} := 273 \text{ (K)} \]

\[ R := 8.314 \text{ (J/mol*K)} \]

\[ P_{\text{std}} := 1.013 \times 10^5 \text{ (Pa)} \]

\[ Q_{\text{Cu}} = \left[ \text{mFR}_{\text{Cu}} \cdot R \left( \frac{T_{\text{std}}}{P_{\text{std}}} \right) \right] \left(1 \times 10^6 \right) \]

\[ Q_{\text{Cu}} = 4.682 \text{ (SCCM)} \]

Flow Summary:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molar Flow Rate (mol/min)</th>
<th>Volume Flow Rate (SCCM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>mFR$_{\text{H}_2} = 0.031$</td>
<td>$Q_{\text{H}_2} = 700$</td>
</tr>
<tr>
<td>IPA - Propanol</td>
<td>mFR$_{\text{IPA}} = 0.013$</td>
<td>$Q_{\text{IPA}} = 300.053$</td>
</tr>
<tr>
<td>bis Cu(II) hfac</td>
<td>mFR$_{\text{Cu}} = 2.089 \times 10^{-4}$</td>
<td>$Q_{\text{Cu}} = 4.682$</td>
</tr>
<tr>
<td>Grand Totals</td>
<td>mFR$<em>{\text{tot}} := mFR</em>{\text{H}<em>2} + mFR</em>{\text{IPA}} + mFR_{\text{Cu}}$</td>
<td>$Q_{\text{tot}} := Q_{\text{H}<em>2} + Q</em>{\text{IPA}} + Q_{\text{Cu}}$</td>
</tr>
<tr>
<td></td>
<td>mFR$_{\text{tot}} = 0.045$</td>
<td>$Q_{\text{tot}} = 1.009 \times 10^3$</td>
</tr>
</tbody>
</table>
Partial Pressures:

Knowing the above information, it is possible to calculate the partial pressures exerted by each component as a function of the injector and/or chamber pressure.

Here, partial pressure = \( \frac{\text{molar flow rate}}{\text{injector/reactor pressure}} \times \text{(total molar flow rate)} \)

First, however, it is necessary to enter the respective pressures of the injector and the reactor:

\[
P_{\text{inj}} = 7.72 \quad \text{(Torr)} \quad P_{\text{rot}} = 1.0 \quad \text{(Torr)}
\]

Hydrogen:

\[
P_{\text{h}_2,\text{inj}} = \frac{m\text{FR}_{\text{h}_2,\text{inj}}}{m\text{FR}_{\text{tot}}} \quad P_{\text{h}_2,\text{rot}} = \frac{m\text{FR}_{\text{h}_2,\text{rot}}}{m\text{FR}_{\text{tot}}}
\]

\[
P_{\text{h}_2,\text{inj}} = 5.379 \quad \text{(T)} \quad P_{\text{h}_2,\text{rot}} = 0.697 \quad \text{(T)}
\]

Propanol:

\[
P_{\text{ipa, inj}} = \frac{m\text{FR}_{\text{ipa, inj}}}{m\text{FR}_{\text{tot}}} \quad P_{\text{ipa, rot}} = \frac{m\text{FR}_{\text{ipa, rot}}}{m\text{FR}_{\text{tot}}}
\]

\[
P_{\text{ipa, inj}} = 2.305 \quad \text{(T)} \quad P_{\text{ipa, rot}} = 0.299 \quad \text{(T)}
\]

bis Cu(II) hfac:

\[
P_{\text{Cu, inj}} = \frac{m\text{FR}_{\text{Cu, inj}}}{m\text{FR}_{\text{tot}}} \quad P_{\text{Cu, rot}} = \frac{m\text{FR}_{\text{Cu, rot}}}{m\text{FR}_{\text{tot}}}
\]

\[
P_{\text{Cu, inj}} = 0.036 \quad \text{(T)} \quad P_{\text{Cu, rot}} = 0.005 \quad \text{(T)}
\]

Gas Densities:

It is now possible to calculate the densities of each gaseous component in the injector as a function of both pressure and temperature inside the injector.

First, however, it is necessary to enter the temperature of the injector:

\[
T_{\text{inj}} = 373 \quad \text{(Kelvin)}
\]

Hydrogen:

\[
\rho_{\text{h}_2,\text{inj}} = \frac{\text{MW}_{\text{h}_2}}{1000} \left( \frac{P_{\text{h}_2,\text{inj}}}{760} \right)^{\frac{1}{1.013 \times 10^5}}
\]

\[
\rho_{\text{h}_2,\text{inj}} = 4.62 \times 10^{-4} \quad \text{(kg/m}^3\text{)}
\]

Propanol:

\[
\rho_{\text{ipa, inj}} = \frac{\text{MW}_{\text{ipa}}}{1000} \left( \frac{P_{\text{ipa, inj}}}{760} \right)^{\frac{1}{1.013 \times 10^5}}
\]

\[
\rho_{\text{ipa, inj}} = 0.006 \quad \text{(kg/m}^3\text{)}
\]

bis Cu(II) hfac:

\[
\rho_{\text{Cu, inj}} = \frac{\text{MW}_{\text{Cu}}}{1000} \left( \frac{P_{\text{Cu, inj}}}{760} \right)^{\frac{1}{1.013 \times 10^5}}
\]

\[
\rho_{\text{Cu, inj}} = 7.39 \times 10^{-4} \quad \text{(kg/m}^3\text{)}
\]

Thus, the overall density of the complex gas within the injector can be found as follows:

\[
\rho_{\text{tot}} = \rho_{\text{h}_2,\text{inj}} + \rho_{\text{ipa, inj}} + \rho_{\text{Cu, inj}} \quad \rho_{\text{tot}} = 0.007 \quad \text{(kg/m}^3\text{)}
\]
Complex Gas Viscosity:
The following computations assume the complex gases can be modeled as hard spheres.

Step 1: Define the mass and estimate the molecular diameter of each molecule.

- **Hydrogen:**
  \[ m_{h_2} = 3.3 \times 10^{-27} \text{ (kg)} \]
  \[ d_{h_2} = 2.74 \times 10^{-10} \text{ (m)} \]

- **Isopropyl Alcohol:**
  \[ m_{ipa} = 99.62 \times 10^{-27} \text{ (kg)} \]
  \[ d_{ipa} = 5.0 \times 10^{-10} \text{ (m)} \]

- **bis Cu(II) hfac:**
  \[ m_{Cu} = 795 \times 10^{-27} \text{ (kg)} \]
  \[ d_{Cu} = 1.20 \times 10^{-10} \text{ (m)} \]

Step 2: Given the molecular diameter and injector temperature, it is now possible to estimate the viscosity of each of the individual constituents of the complex gas.

Aside: It is first necessary to define Boltzman’s constant as: 
\[ k = 1.38 \times 10^{-23} \text{ (N\cdot m^2/s)} \]

- **Hydrogen:**
  \[ \mu_{h_2} = \frac{2}{3\pi} \left( \frac{1}{d_{h_2}} \right)^2 \left( \frac{m_{h_2} k T_{inj}}{\pi} \right)^{0.5} \]
  \[ \mu_{h_2} = 6.57 \times 10^{-6} \text{ (N\cdot m^2/s)} \]

- **Isopropyl Alcohol:**
  \[ \mu_{ipa} = \frac{2}{3\pi} \left( \frac{1}{d_{ipa}} \right)^2 \left( \frac{m_{ipa} k T_{inj}}{\pi} \right)^{0.5} \]
  \[ \mu_{ipa} = 1.08 \times 10^{-5} \text{ (N\cdot m^2/s)} \]

- **bis Cu(II) hfac:**
  \[ \mu_{Cu} = \frac{2}{3\pi} \left( \frac{1}{d_{Cu}} \right)^2 \left( \frac{m_{Cu} k T_{inj}}{\pi} \right)^{0.5} \]
  \[ \mu_{Cu} = 5.31 \times 10^{-6} \text{ (N\cdot m^2/s)} \]

Step 3: Calculate the viscosity of the complex gas according to Wilke’s semi-empirical formula:

Define appropriate constants:
- \[ i = 1 \ldots 3 \]
- \[ j = 1 \ldots 3 \]
- \[ M_i = m_{h_2} \]
- \[ \mu_i = \mu_{h_2} \]
- \[ M_j = m_{ipa} \]
- \[ \mu_j = \mu_{ipa} \]
- \[ M_3 = m_{Cu} \]
- \[ \mu_3 = \mu_{Cu} \]

Define the interim equation:
\[ \phi_{i,j} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-\frac{5}{2}} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{4} \right] \left( \frac{M_i}{M_j} \right)^{25/2} \]

Define the molar fractions:
- \[ x_i = \frac{m_{FR_{h_2}}}{m_{FR_{tot}}} \]
- \[ x_2 = \frac{m_{FR_{ipa}}}{m_{FR_{tot}}} \]
- \[ x_3 = \frac{m_{FR_{Cu}}}{m_{FR_{tot}}} \]

Define the complex viscosity:
\[ \mu_{tot} = \sum_{i=1}^{3} \frac{x_i \mu_i}{\sum_{j=1}^{3} x_j \phi_{i,j}} \]

Thus, the overall viscosity of the complex gas within the injector is:
\[ \mu_{tot} = 8.42 \times 10^{-6} \text{ (N\cdot m^2/s)} \]
Injector Tube Characterization:

1) Calculate the volumetric flow rate within the injector:

\[ \delta = \text{expansion coefficient such that:} \]
\[ \delta := \left( \frac{T_{\text{inj}}}{273} \right) \left( \frac{760}{P_{\text{inj}}} \right) \]
\[ \delta = 134.506 \quad \text{(No Units)} \]

\[ Q_{\text{inj}} := b Q_{\text{tot}} \]
\[ Q_{\text{inj}} = 1.35 \times 10^5 \quad \text{(cm}^3/\text{min)} \]

2) Find the flow velocity:

a. Recall that: \( Q = V \times A \) and as such \( V = Q/A \)

b. We must convert \( \text{cm}^3/\text{min} \) to \( \text{m}^3/\text{s} \) as follows:

\[ Q'_{\text{inj}} := \left( \frac{1}{60 \times 10^6} \right) Q_{\text{inj}} \]
\[ Q'_{\text{inj}} = 0.002 \quad \text{(m}^3/\text{s)} \]

c. Injector tube characteristics:

Inside diameter: \( D_{\text{inj}} := (42) - (0.0254) \) \( D_{\text{inj}} = 0.011 \quad \text{(m)} \)

Cross sectional area: \( A_{\text{inj}} := \frac{\pi D_{\text{inj}}^2}{4} \)
\[ A_{\text{inj}} = 8.93 \times 10^{-3} \quad \text{(m}^2) \]

\[ V_{\text{inj}} := \frac{Q'_{\text{inj}}}{A_{\text{inj}}} \]
\[ V_{\text{inj}} = 25.199 \quad \text{(m/s)} \]

3) Calculate the Reynolds Number to characterize the flow as Laminar or Turbulent:

\[ \rho_{\text{tot}} = 0.007 \quad \text{(kg/m}^3) \]
\[ V_{\text{inj}} = 25.199 \quad \text{(m/s)} \]
\[ D_{\text{inj}} = 0.011 \quad \text{(m)} \]
\[ \mu_{\text{tot}} = 8.42 \times 10^{-6} \quad \text{(N} \cdot \text{s/m}^2) \]
\[ P_{\text{inj}} = 7.72 \quad \text{(Torr)} \]
\[ T_{\text{inj}} = 373 \quad \text{(K)} \]

\[ Re_{\text{inj}} := \frac{\rho_{\text{tot}} \cdot V_{\text{inj}} \cdot D_{\text{inj}}}{\mu_{\text{tot}}} \]
\[ Re_{\text{inj}} = 228.001 \]

if \( < 2300 \) \( \rightarrow \) Laminar
if \( > 2300 \) \( \rightarrow \) Turbulent
Injector Plate Characterization:

1) Let

- \( n \) = number of holes in the plate
- \( L \) = length of hole (thickness of plate)
- \( d \) = hole diameter (entered in inches)
- \( a \) = area of each hole
- \( a_{\text{tot}} = n \cdot a = \text{total area of all holes} \)

\[
\begin{align*}
  n & := 56 \\
  L_{\text{hole}} & = (0.125) - (0.0254) \\
  d_{\text{hole}} & = (0.020) - (0.0254) \\
  a_{\text{hole}} & = \frac{\pi \cdot d_{\text{hole}}^2}{4} \\
  a_{\text{tot}} & = n \cdot a_{\text{hole}} \\
  L_{\text{hole}} & = 0.003 \quad \text{(m)} \\
  d_{\text{hole}} & = 5.0 \times 10^{-4} \quad \text{(m)} \\
  a_{\text{hole}} & = 2.07 \times 10^{-7} \quad \text{(m}^2\text{)} \\
  a_{\text{tot}} & = 1.139 \times 10^{-5} \quad \text{(m}^2\text{)}
\end{align*}
\]

2) Calculate average gas velocity in each hole and its corresponding Reynolds Number:

\[
\begin{align*}
  V_{\text{hole}} & := \frac{Q_{\text{inj}}}{a_{\text{tot}}} \\
  V_{\text{hole}} & = 198.444 \quad \text{(m/s) in each hole} \\
  Re_{\text{hole}} & := \frac{\rho_{\text{tot}} \cdot V_{\text{hole}} \cdot d_{\text{hole}}}{\mu_{\text{tot}}} \\
  Re_{\text{hole}} & = 85.5
\end{align*}
\]

3) Having laminar flow allows simple computation of flow losses sustained in the plate:

a. Entrance length:

\[
L_e := 0.06 \cdot Re_{\text{hole}} \cdot d_{\text{hole}} \quad L_e = 0.003 \quad \text{(m)}
\]

(For laminar flow in holes)

b. Major head losses:

\[
h_{L} := \frac{64}{Re_{\text{hole}}} \left( \frac{L_{\text{hole}} - 0.5 L_e}{d_{\text{hole}}} \right) \left( \frac{V_{\text{hole}}^2}{2} \right)
\]

c. Minor head losses:

- for square edged entrance holes: \( K := 0.5 \) and

\[
h_{L_m} := K \left( \frac{V_{\text{hole}}^2}{2} \right)
\]

d. Total head losses:

\[
h_{L_t} := h_L + h_{L_m} \quad h_{L_t} = 6.416 \times 10^{-4} \quad \text{(m}^2\text{/s}^2\text{)}
\]

4) Now use the energy equation to evaluate the pressure drop across the injector plate by examining flow between two points just inside the ends of each hole:

Thus:

\[
V_1 = V_2 = 0 \\
\frac{a_1}{a_2} = 2 \quad \text{(Laminar flow)}
\]

Resulting in:

\[
\Delta P_{\text{plate}} := \rho_{\text{tot}} \cdot \left( h_{L_t} \right) \left( \frac{760}{1.103 \times 10^6} \right) \quad \Delta P_{\text{plate}} = 3.159 \quad \text{(Torr)}
\]

** where the user defined pressure difference is = \( P_{\text{inj}} - P_{\text{rot}} = 6.72 \quad \text{(Torr)} \)

Note:

Iterations must be performed between the injector pressure and the pressure drop across the plate as indicated above. When these two values are equal, the total coefficient of expansion and temperature changes are valid.

Figure 3.9f. Injector flow analysis - page 6.
Temperature Effects of Adiabatic Free Expansion:

Important assumptions:

a) The temperature of the gas on the back side of the injector plate = T_{inj}

b) The expansion coefficient of $\delta = 134.506$ inside the injector is still valid.

1) Hydrogen:

\[ C_P := 14180 \quad C_v := 10060 \quad \gamma_{h2} := \frac{C_P}{C_v} \quad \gamma_{h2} = 1.41 \]

The governing equation for this thermodynamic effect is:

\[ T_{h2, rot} := T_{inj} \left( \frac{P_{rot}}{P_{inj}} \right)^{\gamma_{h2}-1} \]

\[ T_{h2, rot} = 205.974 \text{ (Kelvin)} \]

2) Propanol:

For a polyatomic "gas"

\[ \gamma_{poly} := \frac{4}{3} \]

\[ T_{ipa, rot} := T_{inj} \left( \frac{P_{rot}}{P_{inj}} \right)^{\gamma_{poly}-1} \]

\[ T_{ipa, rot} = 223.771 \text{ (Kelvin)} \]

3) bis Cu(II) hfac:

For a polyatomic "gas"

\[ \gamma_{poly} := \frac{4}{3} \]

\[ T_{Cu, rot} := T_{inj} \left( \frac{P_{rot}}{P_{inj}} \right)^{\gamma_{poly}-1} \]

\[ T_{Cu, rot} = 223.771 \text{ (Kelvin)} \]
3.2.2.3. Injector plate configurations

The configuration of the injector plate is primarily determined by its composition, thickness, number of holes, and the hole diameter as shown below. Determination of the last two parameters listed are based upon the flow predictions of the mathematical model of the injector plate. Thus far in this research there have been five injector plates designed and modeled. Three of these plates have been used on the CVD reactor, one has been sold to a customer, and the other has not yet been manufactured.
The first injector plate was designed and manufactured prior to the creation of the mathematical model. Therefore, it very closely resembled the injector plates of other CVD reactor manufacturers. This plate, constructed from 0.125" thick aluminum, had four independent gas zones and a total of 56 gas injection holes, each of which were 0.020" in diameter.

The second injector plate (and all other subsequent plates) was designed and manufactured after having created the mathematical model. Through its use, it was determined that there were an insufficient number of holes in the first injector plate and that the holes were too small. The second plate was, therefore, also constructed from 0.125" thick aluminum and also had four independent gas zones, but had a total of 77 gas injection holes, each of which were 0.043" in diameter.

After having run the process for nearly a month, it was determined that the injector source to substrate spacing was too large. Therefore, since the substrate heater/lift assembly was not yet operable, a third injector plate of 1.00" thick aluminum was designed to close up the distance. Additionally, it was also believed that a larger number of holes would be needed since the source would be closer to the substrate and flow field uniformity may be affected (see
results section for discussion on this). Hence, this plate also had four independent gas zones, but had 126 gas injection holes, each of which were 0.0625" in diameter.

The fourth injector plate was designed for a customer application where three different types of gases were to be used simultaneously through six independent gas injection zones. Each of the three gases, however, had to be kept isolated from one another prior to entering the reactor to prevent premature chemical reactions within the injector. In this application, a carrier gas is to be used to help stabilize the flow (i.e., increase the flow rate) of each gas through the injector. This was necessary since each of the reactant gases were introduced in very small quantities, each at different flow rates. Therefore, with each of the gases flowing through only two of the six zones, the number of holes had to be dramatically increased, as shown, to improve the gas distribution within the reactor. This plate, using a slightly modified design, was constructed using 0.250" thick 316L stainless steel (for corrosion resistance) with each zone milled down to 0.125" thick. There were a total of 378 gas injection holes, each of which were 0.0312" in diameter.
The fifth, and final, injector plate has been modeled and designed, but not yet manufactured. This plate was specifically designed for use with the Cu(I) chemistry (the first three were designed for the Cu(II) chemistry) and represents a culmination of all that has been learned throughout the injector development process. This plate will be constructed using 0.500" aluminum with 312 holes distributed among the four zones, each of which will be 0.042" in diameter. It is expected that this plate will yield better films than any of the other plates used thus far in this research.
The following table summarizes each injector plate and the results of the mathematical model performed.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(II)</td>
<td>1000</td>
<td>0.125&quot;</td>
<td>4</td>
<td>56</td>
<td>0.020&quot;</td>
<td>7.82</td>
<td>-157</td>
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<td>4</td>
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<td>0.043&quot;</td>
<td>0.91</td>
<td>-56</td>
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<tr>
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<td>1.00&quot;</td>
<td>4</td>
<td>126</td>
<td>0.063&quot;</td>
<td>0.85</td>
<td>-53</td>
</tr>
<tr>
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<td>Cu(I)</td>
<td>800</td>
<td>1.00&quot;</td>
<td>4</td>
<td>126</td>
<td>0.063&quot;</td>
<td>0.58</td>
<td>-40</td>
</tr>
<tr>
<td>4</td>
<td>Customer</td>
<td>165</td>
<td>0.125&quot;</td>
<td>6</td>
<td>378</td>
<td>0.031&quot;</td>
<td>0.42</td>
<td>-75</td>
</tr>
<tr>
<td>5</td>
<td>Cu(I)</td>
<td>800</td>
<td>0.75&quot;</td>
<td>4</td>
<td>312</td>
<td>0.042&quot;</td>
<td>0.59</td>
<td>-41</td>
</tr>
</tbody>
</table>

Table 3.2. Summary of injector plate modeling.

Each of the injector plates above (except those not yet tested) produced quality Copper films whose properties have continued to improve with each successive design. The transition from Cu(II) to Cu(I) chemistries was driven by ease of process development as well as success at producing Copper thin films with excellent properties, as will be discussed shortly.

Finally, in an attempt to understand the relationship between the hole size in the injector plate as a function of the flow rates of the reactants, a plot was generated using the mathematical model with the flow of Hydrogen being the variable. This plot, shown on the next page, was done for a constant pressure drop of 1.00 Torr across the injector plate using a matrix of holes varying from 50 to 500.
3. CVD Reactor/System Design

The results of this analysis indicate a very smooth, exponentially decaying increase in hole size as the Hydrogen flow rate increases. Additionally, as the number of holes in the injector plate is increased, the hole sizes required for the given pressure drop decrease, as expected. However, it is interesting to note how the decreasing hole size is logarithmic in nature as compared to the linear change in the number of holes. These observations lend additional credibility as to the validity of the mathematical model as the results support qualitative reasoning.

Figure 3.12. Plot of Injector Hole Size vs. Hydrogen Flow Rate for a generic injector plate 0.50" thick with a pressure drop of 1.00 Torr.
4. CVD Reactor/Process Optimization

4.1. Experimental Variables

The design and assembly of this CVD reactor was done for only one reason; to deposit high quality copper thin films that meet, or exceed, the demands of the semiconductor industry. Accordingly, a major part of the design effort was devoted to having as many experimental variables as possible available for the process engineer to work with. This meant that the system needed to be very flexible in its hardware and software configurations, and the ease with which process variables could be changed.

The results of this effort yielded the following experimental parameters available to both the process and equipment engineers: injector metering valve configuration, injector plate design, chemistry of the precursor, source-substrate spacing, substrate temperature, gas flow rates (this includes gas concentrations), plasma use or non-use and its associated power level, process pressure, and the injector/vaporizer temperatures.

The injector metering valve configuration controls the flow of reactants to each of the four zones (six in the case of the customer design) behind the injector plate. Each of these concentric zones are centered over the substrate at increasing radii and affect the growth rate [deposition] of
the film beneath them. For example, if the process engineer determines that the reactants are being depleted near the edge of the substrate causing non-uniform deposition of the film, increasing the flow rate through the third or fourth zones may solve this problem. Another film property which can be controlled using these valves is film composition across the substrate in cases where different gases are used in each zone. The six zone injector is being used in this manner. Zones one and four inject gas A, zones two and five inject gas B, and zones three and six inject gas C (numbered from the inner-most zone).

The injector plate design is the next obvious variable in the development of the film deposition process. This subject has already been covered in great detail in the previous chapter. However, despite all of the effort which has been given into the design, modeling, and manufacturing of this crucial part of the injector, it is ultimately the process engineer that must deposit the films. If the adjustment of other process variables has been unsuccessful in producing quality films, then the injector plate must be suspected of improper performance and examined more closely.

Deposition of any CVD film requires a chemical precursor or gas molecule containing the element(s) to be deposited. This thesis concentrated on the deposition of
copper thin films using Cu(I) and Cu(II) chemistries as previously described. The availability of two different chemistries gave the process engineer yet another variable to work with, the results of which will be discussed later.

Source to substrate spacing is another key variable in the development of any film deposition process, including CVD applications. The reason for this is that gases introduced into the reactor immediately begin to diffuse from their point of introduction, especially at lower process pressures. Complete diffusion occurs at a distance from the point of introduction called the diffusion length. Therefore, by placing the substrate surface at the proper distance form the source, one may achieve optimum film characteristics. The sensitivity to this spacing is highly process dependent, but is typically on the order of optimum distance ±0.125 inches.

Substrate temperature is one of the most crucial parameters in thin film deposition, regardless of deposition method. This temperature dependency is due to the physical and chemical reactions which cause the film to grow. In CVD processes, for example, if the substrate temperature is too low then the chemical reaction taking place at the substrate surface will not be given enough activation energy to break down the molecule; the net results of which will be a low
deposition rate and less than desirable film qualities such as surface roughness, reflectivity, and poor step coverage. On the other hand, if substrate temperatures are too high, the molecule is given so much energy that it may completely dissociate leaving chemically reactive species which may adhere to the deposited film causing high levels of impurities, poor reflectivity, abnormal grain growth, and high film resistivity. Both cases result in a worthless film. Therefore, it is imperative that the process engineer find and maintain the optimum substrate temperature and reproduce it from run to run.

The next experimental parameter that was made available to the process engineer was independent control of gas flow rates. The gases provided on this system included Hydrogen, Nitrogen, and Argon. Both the Hydrogen and Nitrogen were used to provide additional reactive ion species to aid in the chemical decomposition and neutralization of the left-over hfac and/or tmvs ligands which are the by-products of these Metal Organic CVD (MOCVD) processes. The Argon, however, was provided for plasma generation, as is done in sputtering. This plasma, which most useful for the Cu(II) process, helps to create a larger number of reactive Hydrogen and/or Nitrogen ions which assist in increasing the overall deposition rate. Having control over the flow rates
of these gases allows the process engineer to adjust the concentration of these ions to the point where supply and demand are in equilibrium.

The use of a high energy plasma containing reactive ion species, as is done in sputtering and Plasma Assisted/Enhanced CVD, tends to reduce the substrate temperatures required to achieve quality film deposition by providing an additional source of energy to the reactants. Additionally, this plasma also produces ions which act as catalysts to the reaction, thus increasing deposition rates and yield.\textsuperscript{48-49}

The process engineer, therefore, by adjusting plasma power levels (ie. ion concentration and energy) has yet another method of providing control over what is happening within the reactor. In cases where the plasma is not used, the process is simply reduced by that variable and becomes what is known as traditional thermal CVD.

Process pressure is another parameter which directly affects the performance of CVD reactors.\textsuperscript{50} The introduction to this thesis alluded to pressure ranges and how they affect the gas flow characteristics of the reactor. For example, at sufficiently low pressures, the mean free path of each molecule is so high that the molecule tends to collide with its surroundings more frequently than with another molecule. This molecular type flow indicates that
there are far fewer reactant molecules available and that they will have a tendency to randomly diffuse throughout the reactor. These characteristics obviously affect deposition rate and are the major reasons why most CVD processes rarely operate at pressures below 0.5 Torr. Higher process pressures, on the other hand, are those where the molecules have very small mean free paths and collide much more often with each other than with their surroundings. In this pressure regime the gas tends to exhibit laminar flow in a properly designed reactor, which is highly desirable. However, these desirable flow characteristics come at the expense of higher levels of impurities which affect film quality. The idea then, is to find a pressure which is high enough to yield acceptable deposition rates and flow characteristics and low enough to prevent high levels of impurities.

Last, but not least is the temperature of the vaporizer and injector assemblies. The only function of the vaporizer is to convert the incoming liquid precursor into a gaseous vapor. This requires that its temperature be above the vaporization temperature and below a temperature which would cause premature decomposition of the molecule. Similarly, the injector temperature must also be kept within the same range. Should any part of the injector fall below the
vaporization temperature, the gaseous vapor will condense on that surface and create localized puddles of precursor which may or may not re-vaporize. When this occurs, fluctuations in the net flow rate of reactants into the process chamber will result, the effects of which will be non-uniform deposition characteristics and a complete loss of process control.

Each of the nine process variables presented here will ultimately affect the quality of the resulting film. However, the combination and characterization of the effects of each of these parameters as they relate to the others would require thousands of deposition runs and would present an insurmountable task. Therefore, statistical methods have been developed which attempt to correlate the relations among several variables and provide the user with an output to assist in process optimization. This method is called "Design of Experiments," or DOE.

4.2. Design of Experiments, DOE

Process development is often a difficult and extremely time consuming task. The source of this difficulty lies within the large number of variables that affect the overall outcome of the experiment and the possibility that many of them are related (similar to a set of coupled differential
equations). Therefore, methods have been developed by statistical theorists which enable correlation of the effects of several process variables on the outcome in a minimum number of trials.

ECHIP version 6.0, a DOE software package, was employed in this research, at least in part, to help reduce the number of trials needed to characterize the performance of this reactor. Its use required the definition of each process variable of interest and the desired results. It then produced an experiment consisting of a set of trials to be performed by defining the process parameters to be used in each trial. Once these trials were performed, the film results were entered into the computer and the entire experiment was then analyzed.

The entire matrix of process parameters and results enabled the generation of two and three dimensional response surfaces (see figures 4.1 & 4.2) which indicate how the film properties changed in response to a change in one, or more, of the process variables. Once in the ballpark, fine tuning of the process took very little time and was performed on a more "trial and error" basis.
Figure 4.1. A 2-D response field of resistivity versus deposition temperature and pressure.

Figure 4.2. A 3-D response field of resistivity versus deposition temperature and pressure.
4.3. Methods of Film Analysis

Gathering the necessary data for film analysis and characterization can be performed in several ways. The major methods of film analysis utilized in this research included resistivity, uniformity and gap fill measurements. However, several other film properties of interest are still being investigated at this time under a continuing CVD process development program at CVC Products.

Resistivity and uniformity were measured using a four point probe and a Dektak model IIA profilometer. The four point probe was first used to measure the sheet resistance of the film at specified locations on the surface of the substrate. This is done by passing a known electric current through the film from the two outer probes and measuring the voltage necessary to cause that amount of current to flow using the two inner probes. These voltage and current measurements are then used to calculate the resistivity of the film (after the film thickness has been determined) using the equation below:\(^{51}\)

\[ \rho = (CF)(t) \left( \frac{V}{I} \right) \]  

(4.1)
where \( \rho \) is the resistivity (\( \mu \Omega \cdot \text{cm} \)), CF represents the Correction Factor (which is dependent upon the probe spacing and location relative to the edges of the substrate, here CF=4.5324 provided measurements are not taken close to the edge of the substrate), \( t \) is the thin film thickness (m), \( V \) is the measured voltage (mV), and \( I \) is the applied current (mA). The bulk resistivity of copper is 1.678 \( \mu \Omega \cdot \text{cm} \) with acceptable levels of resistivity for this application being below 1.80 \( \mu \Omega \cdot \text{cm} \).

The Dektak profilometer is then used to ascertain the exact film thickness at one or more of the same locations used for resistivity measurements (within the measuring accuracy of the equipment) by measuring a physical step at those points on the wafer. The steps are made by either peeling off a section of the film using a piece of tape or by placing a razor blade on the substrate prior to depositing the film. In the latter case, the razor blade is removed from the substrate after processing leaving a region on the substrate with no deposition.

Next, using the actual known resistivity of the film, one may back substitute each of the voltages obtained earlier to calculate the thickness of the film at each of the specified locations as indicated below:
4. CVD Reactor/Process Optimization

\[ t = \frac{\sqrt{I}}{CV} \]  (4.2)

Following this, the uniformity of the deposited film can be quickly obtained in one of several ways. One way is to use the maximum, minimum, and mean values of the film thickness in the following equation:

\[ \frac{(\text{Max} - \text{Min})}{2 \cdot \text{Mean}} \times 100 = \% \text{Uniformity} \]  (4.3)

Another method is to use statistical analysis by determining the mean thickness of the film and the standard deviation of that thickness. Finding the percentage of film uniformity is then a function of the desired level of confidence in the measurement. Each of these two methods are well known and each is accepted by industry.

Gap fill measurement of a deposited film is done using a patterned wafer. A patterned wafer is a substrate upon which gaps, which are most often holes, have been placed on the surface of the substrate. These holes are identical to those that will play the role of multi-level interconnects between the adjacent metallic layers of a semiconductor device and are typically 0.25 - 1.0 microns \((10^{-6} \text{m}=10,000\text{Å})\) wide. After deposition, a test wafer is cleaved which exposes several of these holes in cross section. Then,
using a Scanning Electron Microscope (SEM), a picture of these holes can be taken and the degree to which they have been filled can be measured; this is known as gap fill.

Each of the three film characteristics obtained are then used to classify the overall process run. In this research, the order in which the properties were optimized was resistivity, followed closely by gap fill, and then thickness uniformity. The reasons for this hierarchy are as follows: first, accurate measurements of uniformity cannot be obtained without good film resistivity measurements; second, even with acceptable resistivity, if the gaps are not properly filled then the film is useless for interconnects; and third, the thickness uniformity can be adjusted as an independent variable at a later time using the multi-zone capabilities of the injector. However, if any of the three are below standards, it falls to the process engineer to determine the problem and make the appropriate adjustments to the process parameters which affect that film characteristic.
5. Results

5.1. Injector Plate #1

The first injector plate used on the reactor was designed and manufactured prior to the creation of the mathematical model, as previously stated. Therefore, it very closely resembled the injector plates of other CVD reactor manufacturers. This plate was constructed from 0.125" thick aluminum and had four independent gas zones with a total of 56 gas injection holes, each of which were 0.020" in diameter.

Very shortly after reactor start-up, it was surmised that this plate was causing the Cu(II) hfac precursor to condense, and possibly freeze, as it emerged into the reactor. This problem was identified by the appearance of spotting on the film as the droplets and/or crystals of precursor landed on the substrate and re-vaporized leaving copper and a significant level of contaminants behind. The contaminant levels were not specifically quantified, but were apparent in the color of the films and their respective resistivities which were often higher than 1800 $\mu\Omega\cdot\text{cm}$. This result, being three orders of magnitude greater than the target resistivity of 1.8 $\mu\Omega\cdot\text{cm}$, indicated that a major change in the reactor configuration was obviously necessary.
However, the cause for the apparent drop in reactant temperature was unknown until after the mathematical model of the injector plate was completed. Once completed, the model predicted that as the reactants exited the injector plate, they underwent an almost instantaneous decrease in pressure of six to seven Torr, depending upon process flow rates. This large pressure drop was due to the combination of too few injection holes and their small diameter, both of which served to restrict gas flow. Therefore, the resulting adiabatic expansion of the gases caused them to decrease in temperature by approximately 150°C, yielding a net gas temperature of approximately 223°C, more than cold enough to condense and/or freeze the reactants, as hypothesized.

Due to the problems experienced with this injector plate, no significant advances in process development took place in the early stages of reactor operation. However, it did provide process and equipment engineers an opportunity to finish debugging both the hardware and software while awaiting the manufacturing of the second, improved, injector plate.
5. Results

5.2. Injector Plate #2

This plate was also constructed from 0.125" thick aluminum and had four independent gas zones, but had a total of 77 gas injection holes, each of which were 0.043" in diameter. According to the mathematical model, this plate would yield a pressure decrease of approximately 0.81 Torr at maximum flow conditions with a corresponding temperature decrease of 52°C. It was not known at the time of design whether or not this drop in temperature would be too large for the reactants or not. Therefore, the plate was manufactured and tested on the reactor.

The initial results, again using the Cu(II) precursor, were not much better than with the first injector plate. The resistivities obtained were still above 1000 μΩ*cm, but the films were no longer exhibiting the spotting observed with the first plate. With this problem taken care of, it was decided that a design of experiments could be performed to narrow the field of process variable combinations in an effort to reduce the film resistivity.

The first DOE involved three process parameters: substrate temperatures between 178 and 208°C; plasma power levels between 10 and 45 Watts; and, reactant flow rates between 700 and 1400 SCCM (using the Hydrogen flow as the
changing variable). The results of first the DOE, shown graphically below, indicated that reduced substrate temperatures in conjunction with higher plasma power yielded the lowest values of resistivity. The flow rate shown is that which was indicated as the optimum flow condition by the software. The zone which appears to be boxed in is that where the software is capable of making direct correlation among the process variables and the resistivity of the film. The areas outside of this zone are extrapolated based upon
that data. Note the dotted line in the lower left corner of figure 5.2: these lines indicate the areas in which the calculated response to changes in the variables do not cross through the direct correlation zone, the results of which are provided as a possible projection of the response field for the experimenter's reference.

The second DOE performed with this injector plate, shown below, was done using substrate temperatures between

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Figure 5.2. Graphical plot of resistivity vs. substrate temperature and plasma power (DOE #2).
5. Results

180 and 210°C; plasma power levels between 30 and 90 Watts; and, process pressures between 0.5 and 1.0 Torr. The results this DOE indicate that increased substrate temperature in conjunction with lower plasma power will yield the lowest values of resistivity (the response field shown indicates measured resistivity). Note that this conclusion directly conflicts with the conclusion of the first DOE. One possible cause for this problem may be the indication that there was a lack of fit (noted on the plot) of the response data to the experimental variables. In this case, the lack of fit was most likely caused by failure to complete the entire experiment due to problems encountered with clogging of the precursor vaporizer after 13 of the required 16 runs to complete the experiment.

However, the analysis of the two DOEs performed here seemed to indicate that film quality was very sensitive to changes in the process variables and may not have been very repeatable. Another observation made, outside of the DOEs, was that the deposition rates obtained were considerably lower than expected when compared to other published work. This problem, common in many deposition processes, is most often attributable to large source to substrate spacing. Both of these problems needed to be solved since, in the
semiconductor industry, they can virtually eliminate an equipment manufacturer from competition in the marketplace.
5.3. Injector Plate #3

In response to the problems encountered with plate #2, a thicker injector plate was designed since the substrate heater/lift assembly was not yet operable. This plate featured a 1.00" thick piece of aluminum designed to close up the distance (from 2.125" to 1.25") and also had four independent gas zones. Additionally, it featured 126 gas injection holes, each of which were 0.0625" in diameter.

The increase in the number of holes was necessary since it was believed that by having the substrate closer to the injector plate, problems with deposition uniformity would occur. This type of problem occurs when the substrate is exposed to the reactants inside of the mixing, or diffusion, length as they enter the reactor. In the case of plate #2, the diffusion length was found to be between 1.00" and 1.75", depending upon process pressure and flow rates. With the substrate now 1.25" from the source, the diffusion length had to be reduced to a maximum of approximately 1.00", and was accomplished by placing the holes in the injector plate closer together, resulting in an increased number of holes.

The mathematical model was again used in designing this plate in an effort to avoid problems with temperature
changes due to gas expansion. Accordingly, this plate would yield a pressure decrease of approximately 1.28 Torr with a corresponding temperature decrease of 70°C under maximum flow conditions. This drop in temperature was estimated to be within the tolerable limit of the precursor.

The first process runs performed with the new source to substrate spacing and injector plate were quite promising. The resistivity of the copper films, using the same process parameters as with the previous plate, were between 6.7 and 7.8 \( \mu \Omega \cdot \text{cm} \) and the growth rates of these films were somewhat improved. This being the case, another DOE was set up to vary the plasma power between 15 and 40 Watts and change the flow configuration of the two innermost zones from fully closed to fully open (values between 0 and 1.8 respectively on the metering valves). Other fixed variables were a reactant flow rate of 1400 SCCM and a reactor pressure of 0.5 mTorr.

The results of this DOE, shown graphically on the next page, yielded the best resistivity thus far; 2.38 \( \mu \Omega \cdot \text{cm} \). The DOE predicted that better results were to be obtained by increasing plasma power levels while completely closing the center injection zone and throttling down the second zone to
3/4 open. This DOE gave the first indications that the new injector plate was to prove effective.

However, experimenting continued unsuccessfully for several more weeks trying to obtain resistivities below

![Graphical plot of resistivity vs. injector configuration and plasma power (DOE #3).](image)

Figure 5.3. Graphical plot of resistivity vs. injector configuration and plasma power (DOE #3).

2.0 μΩ*cm (the best obtained was only 2.2 μΩ*cm, more than 29% higher than the literature which claimed resistivities between 1.7-1.9 μΩ*cm)\(^{52}\). Finally, it was decided to change precursor chemistries from the Cu(II) hfac process, one that had never been used by any of the process engineers involved
with this work, to the Cu(I) tmvs chemistry which constituted the backbone of one of the process engineer's research prior to employment with CVC.

Several modifications had to be made to the reactor since this process was more corrosive, more expensive, and more toxic than the Cu(II) process (the main reason for trying Cu(II) in the first place). As a result, most of the changes to the system were related to safety than to the process itself. One of the more advantageous features of the Cu(I) process was that it did not involve the use of an RF plasma. This essentially meant that there was one less process parameter to be concerned with in searching for a low resistivity copper film.

The first few runs were merely duplicates of prior work which had been performed, as previously mentioned. The results, films with resistivities between 1.91 and 3.88 μΩ*cm, were exceptional considering the fact that the process had not yet been optimized! Hence, deposition of a film exhibiting a resistivity below 1.8 μΩ*cm took another month or so and was achieved by determining the optimum substrate temperature for a given set of flow conditions.

Additionally, the earlier problem encountered with low deposition rates was eliminated as rates better than 1000Å
per minute, with good resistivity and repeatable results, were obtained. These results, and the corresponding process parameters, have recently been presented at a VLSI Multilevel Interconnect Conference (VMIC). The published paper and the corresponding poster presentation is included as Appendices A and B of this thesis.

Gap fill and deposition uniformity were the next two film characteristics to be optimized since the resistivity was now within acceptable limits. Shown below is an SEM micrograph of a completely filled via using the process parameters that yielded the results indicated above.

Figure 5.4. SEM micrograph of a completely filled via (representative of an interconnect).
These same process conditions also resulted in film uniformities of better than 2% with a confidence level of 1 sigma. With these results, all of the goals for this research project had been achieved.
5.4. Injector Plate #4

The fourth injector plate (not including the customer application) has been modeled and designed, but not yet manufactured, as previously stated. This plate was specifically designed for use with the Cu(I) chemistry (the first three were designed for the Cu(II) chemistry) and represents a culmination of all that has been learned throughout the injector development process. This plate will be constructed using 0.50" aluminum with 312 holes distributed among the four zones, each of which will be 0.042" in diameter.

The significant increase in the number of injector holes is provided to accommodate the newly adjustable source to substrate spacing, the hardware for which is currently in the process of being installed. The spacing will be then be adjustable between 0.50" and 2.50". The increased spacing is necessary to allow the reactor to be installed as a satellite module on a cluster tool providing clearance for the robot to load and unload the substrates. This union will give an added measure of cleanliness and repeatability to the process. For all of these reasons, it is expected that this plate will yield better films than any of the other plates used thus far in this research.
6. Discussion

6.1. Reactor Optimization

The optimization of the reactor primarily involved the continuous improvement of the injector and substrate heater/lift assemblies. The other components of the system (such as the reactor chamber, vaporizer assembly, and pumping system) were essentially fixed in their design and could only be changed at great monetary expense.

The injector body itself had not been modified in any way throughout this research as it was known, based upon competitive designs, to be functional in its current form. The metering valve configuration, though expensive, was provided to enable the process engineer the capability to tailor the flow into the reactor as required through each of the four independent gas injection zones. The injector plate, however, was specifically designed to be inexpensive and simple to replace as process development dictated.

It came as no surprise to those involved with this research that it took two design changes of the injector plate (the original plus the two modified plates) before the quality of the films was adequate. The mathematical model employed throughout the development of these two improved plates played a major role in their success, the lack of which may have made the end results unobtainable.
6.2. **Process Optimization**

The optimization of the process proved to be a rather difficult, sometimes formidable, task which took more than eight months to perform. Some of the most common problems encountered, aside from the first two injector plates, were usually related to the clogging of the precursor vaporizer. This situation generally led to the inability to reproduce earlier results since a major component of the system had, sometimes unknowingly, changed in time.

However, even after the problems with the vaporizer had been corrected through dilution of the precursor, a great deal of difficulty was encountered when trying to duplicate the published work of other researchers using the Cu(II) chemistry. This lack of reproducibility was most likely caused by differences in the reactor configuration (ie. the injector, heater, and chamber assemblies) from those of the other researchers. Needless to say, a solution to this problem had to be found.

The proposed solution was to try the Cu(I) chemistry, one that would perhaps respond in a positive way to this reactor configuration. This change proved to be successful as better results were immediately obtained with no further
changes in the system. Within one month, additional process work had provided results surpassing industry requirements.

The major reason credited for the successful deposition of low resistivity copper films using the Cu(I) chemistry over the Cu(II) chemistry was that the Cu(I) chemistry does not require an RF plasma and is a much cleaner process. Recall that the presence of an RF plasma greatly increases the complexity of a deposition process making it much more difficult to optimize. In fact, plasma physics researchers are still trying to ascertain exactly what occurs inside an RF plasma and determine how it affects its vacuum chamber environment and how the configuration of the environment affects it.
6.3. Future Research

Though this reactor has already produced high quality copper thin films, a program has been developed to provide for continuous improvement to the reliability and further optimization of the reactor and the films it produces. These improvements include: a new substrate heater/lift assembly; connection to a cluster tool; a new precursor injection plate; and ultimately, an entirely new reactor which is scheduled for completion in December of this year.

The new substrate heater/lift assembly will provide the capability for deposition on substrates up to 8.0" in diameter (the current design is only capable of depositing on substrates up to 6.0" in diameter). It will also enable process engineers to fine tune the source to substrate spacing thus ensuring that the substrate itself does not interfere with the proper diffusion of the reactants as they enter the reactor. Finally, it will provide the necessary clearance, in its lowest position, for a substrate transfer robot to gain access to the reactor when mounted on a cluster tool's Central Wafer Handler, CWH.

Connecting this reactor to a cluster tool CWH will, as previously discussed, provide an extra degree of cleanliness and repeatability to the process. These improvements to the
process will be provided based upon the fact that with a cluster tool, each substrate is degassed and can be exposed to a pre-clean etching process prior to deposition without leaving an evacuated chamber. Additionally, each of these steps are carried out in a completely independent chamber, each with its own pumping system, which eliminates any possibility of cross contamination. Therefore, with each substrate identically prepared, process repeatability and the levels of film contamination are improved dramatically.

The new injector plate is scheduled to be installed at the same time as the new heater/lift assembly. The reasons for this have already been presented in section 5.4 of this thesis. As discussed, this plate is expected to yield exceptional results as it has been specifically designed for the Cu(I) chemistry. The design process was accomplished by making appropriate changes in the mathematical model to account for differences in flow characteristics between the two precursors.

Last, but certainly not least, is the production of an entirely new Copper CVD reactor which has been specifically designed for this process. This project, which was placed on hold prior to the attainment of production-quality copper thin films, is currently underway and scheduled for completion in December of this year. The reactor will not
only incorporate all of the features of the research reactor used here, but will also include substrate rotation and top side pumping. Both of these additions to the process are expected to further increase the quality of the resulting copper thin films.
7. Conclusion

The primary reason for choosing to develop this copper deposition process is that its electrical resistance is lower than either aluminum or tungsten (the two metals currently being used) and is therefore more suitable as a high speed interconnect. Additionally, since the resistance is lower, the power consumption of the copper interconnects will be lower and generate less heat. The combination of these factors will enable semiconductor manufacturers to produce faster, more reliable semiconductor devices. Other film characteristics, such as diffusion and electromigration of these films are still under investigation.

The copper thin films produced during this research have demonstrated excellent resistivity, gap fill, and uniformity in a relatively low cost research reactor. Though there is still a great deal of work to be done, the process is scheduled for integration into a production worthy reactor to be made available to the semiconductor industry within the next year.

The main goal of this research was to design, build, and optimize a CVD reactor capable of producing quality copper thin films for use as multilevel interconnects in semiconductor devices: this goal has been accomplished.
CVD COPPER IN A COMMERCIAL REACTOR:
A COMPARISON OF CU(I) AND CU(II) CHEMISTRIES

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EXECUTIVE SUMMARY

A commercial chemical vapor deposition (CVD) reactor has been developed for incorporation into a MESC-compatible cluster tool. Both Cu(I) and Cu(II) precursor chemistries have been utilized for depositing thin copper films. Film properties were determined by four-point probe, surface profilometer, and scanning electron microscope (SEM). Deposition rates of up to 1000 Å/min have been obtained, with average film resistivities of lower than 2μΩ-cm.

EXTENDED ABSTRACT

A commercial chemical vapor deposition (CVD) reactor capable of utilizing either Cu(I) or Cu(II) β-diketonate chemistries has been developed for incorporation into a MESC-compatible cluster tool. The single wafer, stagnation point flow reactor features six inch heated wafer capacity, direct metering and vaporization of liquid precursor through use of an MKS liquid pump/vaporizer system, reactant introduction to the reactor chamber through a multi-zone injection manifold, optional variable power (up to 300W) rf plasma assist, manual load lock, and computer control interface. Temperature uniformity has been measured to be better than ±1% across the substrate over a wide range of temperatures. The injection manifold was designed for precise tailoring of gas flow characteristics across the substrate, incorporating four concentric independently adjustable zones, each controlled by a metering valve. Film thickness was measured by surface profilometer and SEM. Film resistivities were calculated from four-point probe and thickness measurements.

The Cu(I) precursor (Trimethylvinylsilyl)hexafluoroacetylacetonato Copper (I), or Cu(TMVS)(HfAc) (CupraSelect™ supplied by Schumacher, Inc.) was used in this system for thermal deposition. This precursor was delivered via direct liquid injection into a moderate (60-300 sccm) flow of hydrogen. The liquid precursor delivery rate was typically 0.2 cc/min. This precursor was delivered with and without the co-injection of
trimethylvinylsilane (TMVS). The addition of TMVS to the mixture is known to affect the thermodynamic equilibrium of the disproportionation reaction of Cu(TMVS)(HfAc) via Le Chatlier's principle. The effect of wafer temperature on resistivity and deposition rate for both the case of 20% TMVS/80% Cu(TMVS)(HfAc) (by vol.) mixtures (Figure 1.) and pure Cu(TMVS)(HfAc) (Figure 2.) is shown below. A 50°C shift in temperature was observed between the two chemistries illustrating the thermodynamic suppression of the disproportionation reaction by TMVS. Uniformity was as good as 2% 1σ.

Figure 1. Resistivity and deposition rate as a function of temperature for 80/20 mixture of CupraSelect/TMVS. Optimal films were grown using wafer temperatures ranging from 190-235°C, chamber pressure of 0.5 Torr, H₂ and precursor flow rates of 200 sccm and 0.3 cc/min. Data is based on profilometer (squares) and SEM (circles) measurements. The difference is caused by surface roughness.

Figure 2. Resistivity and deposition rate as a function of temperature for pure CupraSelect/TMVS. Optimal films were grown using wafer temperatures ranging from 160-190°C, chamber pressure of 0.5 Torr, H₂ and precursor flow rates of 200 sccm and 0.2 cc/min.
Hexafluoroacetylacetanato Copper (II), or Cu(HfAc)$_2$, was used to explore plasma enhanced Cu(II) chemistries for the deposition of copper films. The Cu(HfAc)$_2$ is in powder form and must first be dissolved in isopropyl alcohol in order to form a liquid precursor that can be delivered as a vapor. Hydrogen was used as the carrier gas and deposition was enhanced using a low power plasma as reported in other studies. This precursor yielded growth rates between 50-100 Å/min, with resistivities of better than 2.2 µΩ-cm averaged across the wafer. Uniformity was as good as 3% 1σ. Optimal film properties were attained with a substrate temperature of 170°C, chamber pressures of 0.5 to 1.0 Torr, carrier gas flow rate of 1400 sccm, liquid delivery rate of 1.0 cc/min (1.0 g Cu(HfAc)$_2$ / 10.0 cc isopropyl alcohol), and rf plasma power between 15-40 W. Auger analysis showed that films of better than 10 µΩ-cm resistivity had no detectable incorporated carbon, oxygen, or fluorine. Deposition rate, resistivity, and step coverage for plasma assisted Cu(HfAc)$_2$ are shown in Figure 3 below.

Figure 3. Resistivity (●) and deposition rate (■) as a function of temperature for plasma enhanced deposition using Cu(II)(HfAc)$_2$ (left). Wafer temperature: 160°C, chamber pressure: 0.75 Torr, and plasma power: 25 Watts. Step coverage of 0.5 µm trench with 2 to 1 aspect ratio (right).


CVD Copper in a Commercial Reactor: A Comparison of Cu(I) and Cu(II) Chemistries

CVC Products Inc.

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Copper Deposition/Reactor Requirements

- Low Resistivity Films (≤ 1.8 μΩ-cm)
- Excellent Gap Fill (0.25μm gap, 4:1 aspect ratio)
- Good Thickness and Resistivity Uniformity (1% 1σ on an 8" wafer)
- Low Particle and Stress Levels
- Uniform Source Delivery at High Rates without Pre-Decomposition
- Excellent Temperature Control
  - Temperature Uniformity Across Entire Wafer
  - Prevents Condensation or Undesired Decomposition
    - Injection System
    - Reactor Walls
    - Exhaust System
- High Reliability and Reproducibility
Copper CVD Reactor Design

- Single Wafer, Stagnation Point Flow
- MKS Liquid Delivery System (Pump/Vaporizer)
- Temperature Controlled Injector Zones for High Uniformity
  - Patented Multi-Zone Showerhead Injector Scheme, Metering Valves for Flow Adjust
- Up to 300W rf Plasma for Hydrogen (Deposition)
- Stainless Steel Reactor with Silicone Oil Circulation (Metal Seals)
  - Precision Temperature Control Between 40°C and 220°C

Liquid Delivery System
Copper (I) CVD Precursor

- HfAc-Cu(I)-TMVS (CupraSelect™ from Schumacher)
  - \(2 \text{HfAc-Cu(I)-TMVS} \leftrightarrow \text{Cu}^0 + 2 \text{TMVS} + \text{Cu(II)-(HfAc)}_2\)

- Advantages
  - Liquid Precursor Which Deposits Copper at High Rates
  - Deposit Copper of Very Low Resistivity (\(\leq 1.8 \mu\Omega\cdot\text{cm}\))
  - Good Gap Fill at Moderate Deposition 800Å/min

- Disadvantages
  - Low Thermal Stability, High Moisture Sensitivity
Copper (II) CVD Precursor

- Cu(II)-(HfAc)_2/Isopropyl Alcohol Solution
  - Cu(II)-(HfAc)_2 + 2H → Cu⁰ + 2H-(Diketone)

- Advantages
  - Deposit Copper with Excellent Resistivity
    ✓ (≤2.0 μΩ-cm) with H· Radical Assist
  - Inexpensive ($2-3/gram)
  - Thermally Stable, Low-Moisture Sensitivity
  - Good Gap Fill (3:1) at Low Deposition Rates

- Disadvantages
  - Must be Dissolved in a Solvent for Delivery
  - H· Radicals (Plasma) Required for High Rates & Low Resistivity
Copper CVD Results

Obtained with Schmacher’s CupraSelect
- Low Resistivity Copper at Reasonable Rates
- Good Gap Fill and Adhesion,
- Electromigration Under Investigation


4. Sherman.


15. Gadgil.


17. Sherman.


22. Osinski, Hummel, and Cox.

23. Osinski, Hummel, and Cox.


36. Sears and Salinger, p. 45.


38. Gadgil.


43. Halliday and Resnick, p. 486.

44. Fox and McDonald, p. 294.

45. Fox and McDonald, p. 349 & 353.

46. Fox and McDonald, p. 348.

47. Nunn, p. XXX.


