Effects of Deposition Parameters on Thin Film Properties of Si-based Electronic Materials Deposited by Remote Plasma-enhanced Chemical-vapor Deposition

by

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Approved By:

__________________________  ___________________________
Co-chairman of Advisory Committee  Co-chairman of Advisory Committee
To my wife, Niki,

without whose support, this thesis would not have been possible.

The only constant is change.
Biography


He graduated from Carnegie-Mellon University, Pittsburgh, Pennsylvania in December 1984 with a Bachelor's Degree in Metallurgical Engineering and Materials Science. His senior science project was to study the weld structure of Incoloy 903. In January 1985, he entered the Materials Science and Engineering Department of the University of Illinois, Urbana, Illinois as a graduate student, where he worked with Dr. John A. Thornton on reactive magnetron sputtering of VO₂ thin films. Dr. Thornton unexpectedly died in November 1987. After passing the Ph.D. qualifying examination at the University of Illinois, Jeremy transferred to North Carolina State University's Department of Materials Sciences and Engineering to complete his Ph.D. studies with Dr. Gerald Lucovsky, because of the Dr. Lucovsky's research, and the Department's promise to accept the results of his qualifying examination at the University of Illinois. He passed his preliminary examination in May of 1990, and passed his final thesis defense on May 8, 1992.
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ABSTRACT

THEIL, JEREMY ALFRED. The Effects of Deposition Parameters on Thin Film Properties Si-based Electronic Materials Deposited by Remote Plasma-enhanced Chemical-vapor Deposition. (Under the direction of Gerald Lucovsky.)

The motivation of this thesis is to discuss the major issues of remote plasma enhanced chemical vapor deposition (remote PECVD) that affect the properties Si-based thin films. In order to define the issues required for process optimization, the behavior of remote PECVD process must be understood. The remote PECVD process is defined as having four segments: 1) plasma generation, 2) excited species extraction, 3) excited species/downstream gas mixing, and 4) surface reaction. The double Langmuir probe technique is employed to examine plasma parameters under 13.56 MHz and 2.54 GHz excitation. Optical emission spectroscopy is used to determine changes in the excited states of radiating species in the plasma afterglow. Mass spectrometry is used to determine the excitation and consumption of process gases within the reactor during film growth. Various analytical techniques such as infrared absorption spectroscopy, (ir), high resolution transmission electron microscopy, (HRTEM), and reflected high energy electron diffraction, (RHEED), are used to ascertain film properties.

The results of the Langmuir probe show that plasma coupling is frequency dependent and that the capacitive coupling mode is characterized by orders of magnitude higher electron densities in the reactor than inductive coupling. These differences can be manifested in the degree to which a hydrogenated amorphous silicon, a-Si:H, component co-deposition reaction affects film stoichiometry. Mass spectrometry shows that there is an additional excitation source in the downstream glow. In addition the growth of microcrystalline silicon, μc-Si, is correlated with the decrease in the production of disilane and heavier Si-containing species. Chloronium, H₂Cl⁺, a super acid ion is identified for the first time in a CVD reactor. It forms from plasma fragmentation of SiH₂Cl₂, and H₂. Addition of impurity gases was shown not to affect the electron temperature of the plasma.
By products of deposition reactions can affect film properties by post-deposition reactions with the film. In the case of SiO$_2$ film growth, residual H$_2$O is shown to create OH groups within the film by reacting with distorted Si-O-Si bonding groups.
1 Introduction

1.1 Motivation

The purpose of this thesis is to explore the issues involved with the deposition of silicon-based electronic materials by remote plasma-enhanced chemical-vapor deposition (CVD). The process has been developed as a low temperature technique for the deposition of materials such as SiO₂, Si₃N₄, hydrogenated amorphous silicon (a-Si:H), microcrystalline silicon (μc-Si), and selectively deposited epitaxial Si, and there is a need for a systematic understanding of the process. There is a major trend in the microelectronics industry towards process integration through the use of cluster tooling; and single chamber processing, including etching, and film deposition and growth. The microelectronics industry is concerned with processing techniques that have low thermal budgets, processes with a small time and temperature product. Early chemical-vapor deposition reactors used thermal radiation, i.e., large thermal budgets, to initiate the reaction. Plasma-enhanced chemical-vapor deposition (PECVD) emerged as the first CVD alternative to thermal CVD to gain acceptance at the production level in the industry [1.1]. The disadvantage of direct PECVD (glow discharge) is that consistent film properties are sometimes difficult to achieve, and ion bombardment causes surface damage. Remote PECVD has been developed to achieve better deposition/etching chemistry control, and minimal process-induced substrate damage. This thesis will explore the interactions between the gas phase reactions of the remote PECVD process and silicon-based thin films produced.

1.2 Overview

The thesis is organized in the following manner. This chapter introduces CVD in general terms, and describes the specific features of the remote PECVD process. In addition it provides background information for the materials systems described later on. Chapter 2 discusses the design of the two reactors used for this study, and the analytical techniques used to characterize the deposition atmospheres, and the deposited films.
Chapter 3 concentrates on the effect of power, coupling mode, and other gases on the He plasmas that drive the reactions. Chapter 4 examines how SiH₄ interacts with the He plasma and how the products of that interaction affect a-Si:H film growth. Chapter 5 examines how the addition of hydrogen to the plasma affects the gaseous products of the SiH₄ plasma interaction. Chapter 6 discusses the deposition/etching processes of low temperature selective silicon epitaxial growth, and examines the decomposition of SiCl₂H₂ with He and He/H₂ plasmas. Chapter 7 discusses the effect of excitation frequency and nitrogen source gas on the deposition processes for amorphous silicon nitride, Si₃N₄. The effects of deposition by-products on film properties for amorphous silicon oxide, SiO₂, are discussed in Chapter 8. Chapter 9 examines the power coupling into the plasma, downstream gas backdiffusion, and the effect of chamber geometry on heterogeneous and homogeneous reactions.

1.3 Types of CVD Processes

One of the primary classes of deposition techniques used for growing silicon-based electronic materials is chemical-vapor deposition. Chemical-vapor deposition techniques use gaseous precursors to deliver deposition species to a growing film surface. Various methods for exciting precursors used in chemical-vapor deposition systems are thermal energy, photons, and electrically charged particles.

In thermal energy reactors, the energy is imparted into the chamber using lamps or inductive heating coils. Hot-walled reactors heat the gas through chamber surfaces to initiate the reaction, as for example in homoepitaxial film growth by heating silane (SiH₄) to temperatures between 800-1000°C [1.2]. Cold walled reactors heat the substrate to initiate gas decomposition and film growth. The main drawbacks with these processes are the high temperatures to which the substrate is subjected, and reactant and by-product transport, which is limited by the high pressure, typically several hundred Torr. High substrate temperatures permit dopant diffusion, induce thermal stress between layers of
different thermal expansion coefficients, and increase sublimation of high vapor pressure species. The rate limiting step switches between surface diffusion limited rates and gaseous diffusion limited rates around 1 Torr [1.3]. Lowering the operating pressure also decreases the homogeneous reaction rates. For example, in the case of silane decomposition, a-Si:H powder forms at higher pressures.

In some cases a desired reaction may occur thermally only at reasonable rates above the melting point of the substrate. Therefore, other excitation techniques are required to circumvent the temperature barrier. Photo-CVD systems use radiation to excite molecules into higher energy states. Two commonly used procedures are, non-coherent light sources that illuminate the chamber, and lasers for broad and selective area illumination. There is also an indirect photo-CVD technique that uses UV radiation from a Hg lamp to excite Hg atoms within a CVD reactor. The excited Hg atoms impart their electrically stored energy into SiH₄ molecules [1.4,1.5].

1.4 Plasma-enhanced CVD

Plasma-enhanced chemical-vapor deposition uses electric fields to accelerate charged particles in the reactor to impart energy into the deposition precursors. All PECVD techniques involve the plasma excitation of at least some of the gaseous species in order to produce the chemically reactive species that promote low temperature deposition. The one disadvantage of PECVD techniques is that they must be carried out at relatively low pressures (less than a few Torr), so that the plasma glow can be maintained.

Direct PECVD, uses a self-sustained plasma glow to decompose gas precursors that pass through the plasma. Energy is coupled into the plasma via electron accelerations and collisions with neutral particles. The simplest technique involves passing a dc voltage through a low pressure gas to sustain the plasma. However, the electrodes become coated with materials that interfere with passage of the current, such as in a buildup of silicon oxide dielectrics. Alternating current discharges are commonly used to circumvent this
problem. Glow discharge processes were first used by Alt et al. to deposit silicon oxide films in 1963, and amorphous silicon by Sterling and Swann in 1965 [1.6,1.7]. The technique is used in industry today to deposit silicon oxide films for isolation and protective layers on integrated circuits. It is also receiving attention for its use in etching, such as in reactive ion etching and dry etching techniques.

Source gases and diluents are injected into the chamber, usually through a hole in the center of one electrode. The substrate and all of the gases in the deposition chamber are exposed to the plasma leading to several parallel deposition reaction pathways. The large variety of deposition reaction paths makes it difficult to control stoichiometry and purity of the deposited thin films. One exception to this general observation is a direct PECVD process, the Batey-Tierney Process for SiO₂, in which extremely high dilution of the process gases limits precursor formation and the therefore multiple reactions pathways, and leads to formation of stoichiometric, hydrogen-free, device quality thin-films [1.8]. They speculate that heavily diluting the source gas limits silane gas phase insertion reactions by lowering the probability of silane radical/silane collisions [1.9].

The remote PECVD process affords greater control over the deposition chemistry by restricting plasma excitation to a subset of the process gases and thereby reducing the multiplicity of reaction pathways. The physical arrangement of the chamber is such that the process flow is sequential, rather than parallel as in direct PECVD. The process is typically broken down into four segments: 1) plasma generation, 2) active species extraction, 3) downstream gaseous mixing, and 4) substrate surface reactions. A subset of the process gases is excited in a tube located outside the deposition chamber. Plasma-excited species flow from the plasma-generation region into the deposition chamber and mix with the remaining unexcited process gases. The excited species extracted from the plasma tube and the unexcited species injected downstream mix, then react to produce the desired film on the substrate [1.10,1.11]. For the deposition of SiO₂, Si₃N₄, and SiOₓNᵧ alloys,
process gases, such as SiH₄, and Si₂H₆, etc., are injected downstream and are not exposed to the plasma. This limits gas-phase activation of the silanes and minimizes deposition reaction pathways that promote either non-stoichiometry in the Si:O and/or Si:N ratios, or the incorporation of bonded hydrogen in SiH.

The first to propose the remote plasma technique for thin film growth was Helix et al. [1.12]. Meiners was also an early developer of the technique. He wanted a technique that did not subject the substrate to the effects of the plasma sheath when depositing SiO₂ thin films [1.13]. Since then, Lucovsky et al. has used the technique to grow a variety of materials, from dielectric thin films to a-Si:H to selective silicon epitaxy [1.14-1.20]. Tasch et al. have been using low rf power techniques to grow epitaxial films at temperatures as low as 180°C [1.21].

1.5 Background

1.5.1 Plasma Behavior

Because plasma generation is external to the main reactor and is performed in a cylindrical fused silica tube, it is possible to change the power applicator without disturbing other aspects of the reactor geometry. The use of different excitation frequencies allows for tailoring the electron energy distribution function (EEDF), hence the possibility of altering the dominant excitation states of molecular and ionic species. Wertheimer and Moisan have shown that the EEDF depends strongly on the ν/ω ratio, where ν is the electron-neutral collision frequency, and ω is the applied power frequency, (see Fig. 1.1) [1.22]. The ordinate, u, is the electron energy while f(u) is the fraction of electrons in that energy state. They show that low frequency plasmas (curve D, ν/ω→∞) have a larger high energy electron population than high frequency plasmas (curve A, ν/ω→0). High frequency plasmas approximate a Maxwellian EEDF. For example, at 300 mTorr and at an average electron temperature of 3 eV, ν/ω is 51 for the rf discharge, and 0.25 for the microwave discharge. Therefore, the rf discharge is dominated by electron-neutral collisions, and
therefore does not have a Maxwellian EEDF. The microwave discharge, on the other hand, approximates a Maxwellian distribution, i.e., it has a higher fraction of electron-electron collisions. For the same power density, the microwave discharge is characterized by a lower $T_e$ and higher $n_e$ than the rf discharge (Fig. 1.1).

![Plot of the electron density of energy states for different $v/\omega$ values](image)

Figure 1.1- Plot of the electron density of energy states for different $v/\omega$ values [1.22].

1.5.2 Amorphous Silicon Growth

Hydrogenated amorphous silicon thin films were first used in optoelectronic applications such as photovoltaic materials and photosensitive drums for copiers and laser printers. Recently, activity has focused on the development of a-Si:H for large area thin film transistor circuits such as drivers for flat panel displays, where it is necessary for
devices to be fabricated reliably on non-crystalline substrates. The deposition system is an ideal starting point for studying the remote plasma growth process because the gas chemistry is the simplest of all silicon-based thin film systems. Normal growth sequences of a-Si:H by remote plasma techniques involve the flow of pure He through the discharge tube, and the injection of SiH₄ in the reactor to mix with the He afterglow and initiate film growth. The motivation for this study is to understand how the He plasmas excite SiH₄ to form a-Si:H films.

Amorphous silicon growth has been studied for glow discharge processing for several years. The work has concentrated on the production of SiH₂ and SiH₃ radicals and the phenomena dealing with their surface diffusion and incorporation into the Si network. On the basis of their measurement of a strong SiH₃ metastable signal in SiH₄ and Ar discharges, Gallagher et al. proposed that SiH₃ radicals were the chief precursors for a-Si:H film growth [1.23]. Veprek et al. pointed out that SiH₃ cannot undergo insertion reactions, as can SiH₂, which limits network propagation on hydrogen terminated surfaces [1.24,1.25]. In addition, the amount of SiH₂ required for the reported deposition rates seen is lower than the detectability limits of current in-situ techniques. Perrin and Broekhuizen used an excited Hg technique to preferentially produce SiH₃ in ratios of 20-100 to 1 when compared with SiH₂, to study its reaction rates [1.26]. They noted that even though SiH₃ can be used to grow films for this photo-stimulated CVD process, 60% of the SiH₃ is converted into disilane using the surface as a catalyst. They found that the sticking coefficient is much lower for SiH₃ than SiH₂, 0.04 and 0.70 respectively [1.27,1.28]. Tanaka and Matsuda used a movable substrate and confined plasma triode process to measure the growth contributions of various SiHₓ radicals [1.28]. They showed that at temperatures sufficient to remove surface bound hydrogen (>460°C), the sticking coefficient of SiH₃ is estimated at unity, but the sticking probability of SiH₃ drops when the growing surface has a large fraction of H-terminated sites.
Two of the proposed mechanisms for the Si network propagation for a-Si:H films are, 1) insertion of a silane radical by breaking of a surface Si-H bond, and 2) abstraction of H from the surface by atomic H to leave a bare site available for Si incorporation [1.29]. Tsu showed that for the remote plasma process deposition of a-Si:H was dependent upon charged species interacting with the silane [1.30]. By use of a grid that controlled the entrance of charged species into the chamber he was able to modulate the penetration of the plasma into the chamber. He noted that there would be deposition only when the plasma could penetrate past the grid. The results of that work showed that in the remote plasma process it is necessary to use charged particles (electrons) to initiate the deposition reaction.

1.5.3 Microcrystalline Silicon Growth

Microcrystalline silicon can be used as a substitute for a-Si:H in photovoltaic applications since it does not appear to suffer from the Staebler-Wronski effect. It has already been used in the fabrication of LEDs and there is consideration to replace a-Si:H with μc-Si in large array TFT devices because of its higher mobility and doping efficiency [1.31]. The growth techniques include, glow discharge, remote PECVD, and sputtering. The common denominator of these techniques is that they use high concentrations of H₂ in the reaction chemistry [1.31-1.36]. Under the experimental arrangements utilized for growth of μc-Si films, the H₂ content in the reaction gas has ranged from 15% to almost 100% [1.33,1.36].

A μc-Si film is one in which the crystallite size on the order of 50 nm and the crystallite is surrounded by an amorphous silicon network. Evidence of this amorphous silicon network is the Raman band centered about 490 cm⁻¹ in addition to the 520 cm⁻¹ crystalline feature, and the appearance of disordered regions surrounding the crystallites seen in high resolution transmission electron microscopy images [1.37].

Many papers have been written on the mechanisms of a-Si and μc-Si film growth. Tsai et al., among others, has demonstrated that for glow discharge systems it is possible
to reach a high enough hydrogen concentration so that film growth will stop [1.31]. As they lowered the hydrogen content, the results went from no growth to μc-Si deposition, and finally to a-Si:H deposition. Tsai proposed that hydrogen interrupts the normal film growth process by increasing the degree of surface hydrogenation and by removing Si from the network. It has been shown that etching occurs if the H₂:gas phase Si is high enough [1.38]. Nomoto et al. have shown that μc-Si growth is promoted through hydrogen coverage of the Si surface, and that growth zone processes do not account for μc-Si growth [1.39].

1.5.4 Selective Silicon Growth

Selective homoepitaxial growth of silicon is a valuable technique that creates unique opportunities for production of high density circuits by eliminating some photolithographic processing steps. For example, self-aligned techniques for polycrystalline silicon can eliminate several lithographic and etching steps required for producing source and drain junctions. Studies of selective deposition processes date back to the 1970s, and have used processes involving thermal decomposition of halogenated silanes. The initial processes employed temperatures in the range of 800-1000°C. The lower thermal budget of remote PECVD is the reason for using it in a selective silicon technique. In fact, homoepitaxial films have been deposited by Tasch et al. [1.40]. By remotely plasma exciting SiH₄ and H₂ by a He plasma, Tasch, et al. deposited an epitaxial layer as thick as 100Å at temperatures as low as 150°C, and unlimited film thickness at temperatures of 305°C.

A variety of thermal CVD techniques utilizing combinations of H₂, HCl, and partially halogenated silane compounds, have been employed for selective silicon epitaxial growth [1.41,1.42]. Much of the work on the chemistry of the Si/H/Cl system for thermal CVD processes shows that there are competing deposition and etching reactions [1.43,1.44]. However, the high processing temperature (500-850°C minimum) is undesirable for technologies where dopant diffusion and thermally induced stress must be
-10-

minimized, or where heterojunction layers using compound semiconductors have been grown [1.45,1.46].

Low temperature selective epitaxial growth has received much attention [1.47-1.49]. There are two other plasma techniques by which Si has been selectively grown. Baert et al. employed a glow discharge to deposit microcrystalline high conductivity n+ silicon source and drain electrodes for a CMOS device, utilizing SiH₄ and SiF₄ as a source of etchant [1.50]. Yew and Reif used a H₂ plasma with an alternating SiH₄ flow, to switch between Si deposition and etching, and obtained selective high quality epitaxial films at 600°C [1.51]. In all of these processes, selectivity is achieved only within a narrow window of operating conditions between net etching and indiscriminate deposition across the sample surface [1.52].

1.5.5 Silicon Nitride Growth

Silicon nitrides deposited by PECVD is used for passivation and isolation layers, and for constituent layers of gate dielectrics for ULSI circuits, and oxide-nitride-oxide, ONO. They are being developed for use as dielectrics for storage capacitors for dynamic random access memory, DRAM, circuits. Many papers have been written on the topic of silicon nitride film growth by different plasma processing techniques, glow discharge and remote PECVD [1.53-1.63].

Chiang and Hess used rf-powered glow discharge, SiH₄, and both N₂ and NH₃ sources to grow silicon nitride films [1.60]. Using a grounded grid to minimize ion bombardment of the growing film, they found that is was possible to reduce the relative amount of silicon in the films. They attributed the better stoichiometry to selective deposition of Si-containing precursors on the screen. Tsu and Lucovsky found that the Si-N(s) mode is sensitive to the local environment, excess Si-H groups lower the ir absorption frequency below 832 cm⁻¹, and excess N-H groups raise the ir absorption frequency [1.58]. In addition they found that the growth rate decreases with increasing N₂
concentration, but increases with higher NH$_3$ concentrations. Smith has shown that in a radio-frequency, rf, plasma-excited SiH$_4$/N$_2$ deposition atmosphere, there are no homogeneously-generated deposition precursors formed with Si-N bonds [1.53,1.64, 1.65]. However, when operating under conditions below disilane forming silane concentrations and power saturation, the films were Si-H free. However, for an SiH$_4$/NH$_3$ deposition atmosphere, aminosilanes (Si(NH$_2$)$_x$, x=1-4) ions detected for high NH$_3$:SiH$_4$ ratios are believed to contribute as precursor species in the deposition reaction chemistries. Using a triple-filter quadrupole mass spectrometry they were able to separate multi-silane species from multi-aminosilanes [1.65,1.66]. They found that for a 25:1 NH$_3$/SiH$_4$ ratio, SiH$_4$ was converted into other species; disilane at low power levels (3W), and triaminosilanes as the power increased to 18W. Because of the disilane presence at low power, the implication was that SiH$_4$ was activated. They speculated that deposition was driven by the production of the triaminosilanes because the deposition rate and triaminosilane signal tracked one another.

1.5.6 Silicon Oxide Growth

The utility of SiO$_2$ in the microelectronics industry has caused much interest in depositing electronic quality SiO$_2$ thin-films at low temperatures. Plasma-enhanced chemical-vapor deposition (PECVD) techniques have proved encouraging in producing such films, due to lower substrate temperature when compared to pyrolytic CVD techniques. However, one of the main concerns is chemically bonded hydrogen in SiO$_2$ films. For example, it has been shown that films deposited by conventional direct PECVD generally contain between 5 and 10 at.% unintentionally incorporated hydrogen bonded in both Si-H and Si-OH groups [1.67-1.70]. However, the concentration of bonded hydrogen in SiO$_2$ films grown by remote PECVD can be reduced to levels below the range of infrared (ir) detection, less than about 1 atomic % [1.71]. Tsu identified deposition
conditions and specific reaction pathways by which controlled amounts of SiH can be incorporated into the remote PECVD SiO₂ films [1.72].

For remote PECVD SiO₂ depositions, SiH₄ is injected downstream from the plasma region, and plasma excited O₂ or N₂O is used as the source of the oxygen atoms. By a combination of gas injection points, flow rates, and pressure, silane back-diffusion into the plasma region can be minimized. This minimizes deposition reaction pathways that derive from the direct plasma excitation. Tsu et al. identified two pathways for the deposition of the SiO₂ films, and one for a-Si:H: [1.67]

\[
\begin{align*}
(\text{He} + 2\text{O}_2) \rightarrow & \text{SiO}_2 + 2\text{H}_2\text{O} \quad (1.1) \\
(\text{He} + \text{O}_2) \rightarrow & \text{SiO}_2 + 2\text{H}_2 \quad (1.2) \\
(\text{He}) \rightarrow & \text{a-Si:H} + \text{H}_2 \quad (1.3)
\end{align*}
\]

where the starred bracket notation, \((\)\), identifies the plasma excited gases. The a-Si:H reaction (1.3) proceeds only when electrons and inert gas ions are transported out of the plasma generation region into the deposition region [1.72,1.73]. The deposition of oxides on the other hand, does not require electrons or ions to activate the surface deposition reaction. High O₂ concentrations (>2 \% in He), low substrate temperatures (<250°C) and high deposition rates (>1 Å/s) result in ir-observable OH incorporation; whereas higher temperatures (> 250°C), lower O₂ flow rates and lower deposition rates (<0.2 Å/s), minimize or eliminate any OH incorporation during the film deposition, or during the cool-down period [1.71,1.74-1.77]. Such concentrations of O₂ in He, coupled with the flow rate of silane represent O₂/SiH₄ gas ratios close to unity. However, upon prolonged exposure to atmospheric moisture, generally on a time scale of months or years, even these films display measurable ir absorbance in the Si-OH band.

Si-OH groups can be incorporated into the SiO₂ films by either intrinsic or extrinsic pathways [1.75,1.76]. The intrinsic pathways are associated with the heterogeneous chemical reactions responsible for film growth. Extrinsic pathways refer to mechanisms
after film growth has stopped, and can occur during cool-down in the deposition chamber, or outside the chamber upon prolonged exposure to water vapor. An earlier study by Pliskin [1.78] has shown that Si-OH groups can be incorporated in CVD oxides by extrinsic processes, i.e., upon exposure to atmospheric water vapor. Under all of the deposition conditions investigated to date, no evidence has been found to support an intrinsic OH incorporation process that occurs during film deposition.

References


[1.38] J. Theil, Unpublished experimental results show that a 75W rf plasma with 25% H₂ 200 sccm gas flow, and 10 sccm 1% SiH₂Cl₂ + He, (a 500:1 H₂/SiH₂Cl₂ ratio) etches Si wafers.


[1.77] D.V. Tsu and J.A. Theil, Unpublished data.

2 Equipment and Instrumentation

This chapter describes the remote PECVD systems used to grow films and the instrumentation used to examine reactor gases and film properties. The first section examines the different process reactors, types of power supplies, and gas handling equipment used in this thesis. The second section describes the Langmuir probe technique used for plasma characterization, the mass spectrometry used for gas species monitoring, and the optical emission spectroscopy used for examination of the excitation of gaseous species by the plasma. The second section also briefly describes ex-situ film characterization techniques and their purposes. These ex-situ techniques are infrared spectroscopy, transmission electron microscopy, high resolution scanning electron microscopy, reflection high energy electron diffraction, and ellipsometry.

2.1 Deposition Systems

The deposition/analysis system used for this study embodies all of the attributes of a remote PECVD system, but has additional features that permit in-situ analysis of the gas species in the chamber and of excited radiating species. The first subsection describes a narrow diameter chamber, and the plasma tube end grid apparatus used for oxide growth experiments. The second subsection examines a wider diameter chamber used for all other experiments. The third subsection discusses the load-lock and the substrate loading/heating assembly. The fourth subsection describes at the plasma power supplied used to generate the 13.56 MHz and the 2.54 GHz frequency plasmas. The last subsection describes the gas delivery, the gas pumping, and the reactor control systems that make up the majority of the vacuum system components.

2.1.1 Narrow Diameter Chamber

The narrow diameter deposition chamber used for the oxide deposition experiments is constructed of using a 5.1 cm outer diameter (O.D.) x 46 cm long stainless steel (SS)
tube (Fig. 2.1). The plasma is generated in a 32 mm O.D. vitreous silica tube located at
one end of the deposition chamber. The deposition chamber contains of two gas dispersal
rings and three analyzing stations. The gas dispersal rings are single flange-embedded rings
located at 10.2 cm and 35.6 cm downstream from the plasma tube. The three analysis
stations are located at 2.5, 13.4, and 39.4 cm from the end of the plasma tube, positions
#1, #2, and #3, respectively. Each station has three ports: one for mass spectrometer
sampling, one for optical emission spectroscopy (OES), and one for viewing the inside of
the chamber. A 400 l/s turbomolecular pump in the mass spectrometer chamber is used to
pump the deposition chamber and can achieve a base pressure of < 2x10⁻⁷ Torr in the
deposition chamber.

A end grid assembly is installed at the end of the plasma tube in the 5.1 cm
diameter chamber, and is used to control the penetration of charged species into the
chamber. It consists of four 7 cm x 2.5 cm coaxially oriented stainless steel plates and a
#10 stainless steel (SS) screen grid that caps the downstream end of the assembly. Each
piece is electrically isolated from the chamber. The end grid is normally biased in one of
two states, either tied to the ground potential or electrically insulated from the rest of the
chamber. The four stainless steel plates are always held in the floating or "insulated" state.
When the grid is in the grounded state, the plasma after-glow extends beyond the grid into
the chamber; when it is in the floating state, the afterglow is contained behind the grid and
no charged particles penetrate into the deposition region.

2.1.2 Large Diameter Chamber

The large chamber has a 14.9 cm inner diameter and 56 cm length., see Fig. 2.2.
At one end of the chamber is a plasma tube flange in which a 3.2 cm inner diameter fused
silica tube is located on the central chamber axis. Inside the chamber, at 10.2 cm and 35.6
cm from the end of the plasma tube there are two sets of double gas rings for downstream
injection of gases. There are three sampling stations located in the deposition chamber. The
Figure 2.2- Schematic diagram of 15 cm diameter reactor.
first one is located 2.5 cm downstream from the plasma tube flange, position #1. The other
two are located 3.8 cm downstream from the each set of gas dispersal rings. They are
designated as positions #2, and #3 located at 13.4 cm and 39.4 cm downstream,
respectively. Each station has three ports, two horizontal ones with pyrex windows, and a
vertical one to accommodate the sniffer tube for the mass spectrometer. A dedicated 400 l/s
Leybold TMP360H turbomolecular pump services the chamber from a vertically mounted 6
in. flange located 25 cm downstream from the plasma tube. It can achieve a chamber base
pressure of ~3 x 10⁻⁸ Torr.

2.1.3 Load-lock and Sample Loading/Heater Assembly

A load-lock permits the sample to be placed under vacuum without exposure of the
entire chamber to atmosphere. The load lock used in this vacuum system is connected to
the main chamber by a pneumatically operated gate valve. The other end of the load-lock is
sealed upon insertion of the sample loader/heater through a double teflon gasket
differentially pumped seal. The sample loader/heater assembly consists of a polished 91
cm long SS tubular linear feed-through and a 2.5 cm O.D. copper block with a 250 W
lamp and embedded thermocouple. The entire substrate holder and linear feedthrough is
electrically isolated from the rest of the chamber. A 50 l/s Leybold TMP50 turbomolecular
pump pumps the load-lock and the differential seal when it is evacuating the loadlock, but
only the differential seal when the sample is inserted into the chamber.

2.1.4 13.56 MHz Plasma Generator

The rf power antenna is a ten turn 4.45 cm inner diameter copper coil wrapped
around the plasma tube. The coil is soldered to a coaxial connector, and is mounted within
a grounded metal box with two openings of 4.45 cm diameter for the plasma tube. The rf
power is delivered from an rf generator through a coaxial cable via a matching network, (rf
Plasma Products model HFS-251 power supply, and MN-500 matching network). The
antenna is housed in an aluminum and brass box that can be mounted on either chamber by
three axially-centered stainless steel rods.
2.1.5 2.54 GHz Applicator and Generator

The microwave applicator is a commercially available unit that utilizes an ASTEX S-250 power supply capable of broadcasting a 0-250W signal at 2.54 GHz and standard dimension waveguide components for the 2.54 GHz band. The power supply was kept at 170 W for all experiments, because 150W is the minimum power level at which He discharges are stable in the configuration used. The transmission mode in the waveguide is shown in Fig. 2.3 and is denoted as the TE$_{01}$ mode [2.1]. In this mode the E field is transverse to the propagation direction and a single node exists. Therefore the maximum field intensity is in the center of the waveguide along its long cross-sectional dimension and coincides with the center of the plasma tube.

Figure 2.3- Diagram of 2.54 GHz wave propagation within microwave waveguide

The microwave components are arranged as follows. A circulator and a dummy load are mounted on the back of the power supply to prevent back-reflected radiation from reaching the magnetron tube. For mechanical flexibility in power supply mounting, a coaxial cable connects the circulator to two 50 db directional couplers that are used to monitor the forward and reflected power from the applicator. A network matching three-stub tuner connects the directional couplers with the applicator. The plasma tube passes
through the 3.8 cm dia. opening in the applicator. The opening has two wings that match the wavelength node distance. The applicator waveguide is supported by a rigid channel-bar Al stock mounting frame to prevent movement of the applicator and damage to the plasma tube. The gas stem nipple of the plasma tube is supported by a frame mounted holder that permits alignment along three axes.

2.1.6 Pumping and Gas Delivery Systems

The process pumping system is a Leybold WSU251 Roots blower backed by a Leybold D95B rotary vane pump, both filled with PFPE (silicone-based) oils. The rotary vane pump exhausts gases into a double stage pumped-water scrubber designed by D. V. Tsu and P. D. Richard. The scrubber eliminates silane by reacting it to water to form particulate SiO₂.

The gas delivery system has seven parallel gas lines, each consisting of an interchangeable tank valve connector, a line cross-purge assembly, a high pressure stainless steel regulator, and a MKS 2259B mass flow controller. All lines tie into a gas manifold that mixes and distributes gases to the plasma tube or to one of two downstream gas dispersal ring lines. The two gas dispersal ring lines are each connected to one of two sets of downstream dispersal rings. One gas dispersal ring line is dedicated to delivery of gas mixtures containing silane. The purpose of parallel downstream gas dispersal lines is to prevent the reaction of silane before it reaches the reactor. The process pressure is measured by an MKS capacitance manometer which controls a downstream throttle valve.

The system status is monitored and controlled by a lightboard located outside the processing reactor room to allow remote control. The light board consists of a TTL driven 5V-isolated indicator board that shows the state of switches internal to the lightboard. Each light corresponds to either a valve or a pump in the system. The logic is controlled by a series of 110 VAC relays and toggle and deadman switches that permit only certain sequences of pump and gate valve operation. The system allows an orderly shutdown and
reset of chamber components upon power interruption. In addition, a delayed vent control overseer circuit is installed to permit remote operation of the TMP360 turbomolecular pumps without premature release of vent gases.

2.2 Instrumentation

This section describes the techniques used for in-situ characterization of the plasma afterglow and the reactor gases. In the first subsection a Langmuir probe system is used to characterize the plasma, primarily the electron temperature, $T_e$, and electron density $n_e$. Mass spectrometry is used to examine the ions and neutral species formed in the reactor and is described in the second subsection. The third subsection briefly describes the purpose and operation of an optical emission spectroscopy unit. The final subsection examines the techniques used for ex-situ film characterization.

2.2.1 Langmuir Probe Analysis

The simplest way to determine plasma parameters is through the use of Langmuir probe techniques. By careful analysis of the current-voltage (I-V) curve, it is possible to derive the space charge potential ($V_s$), the floating potential ($V_f$), the electron density ($n_e$), and the electron temperature ($T_e$). In special cases, information about the electron energy distribution function (EEDF) can also be determined. The technique involves placing a conductive probe of known geometry into the glow and recording the current detected by the probe as its potential is varied with respect to the plasma [2.2]. The most common probe configurations are the double and single cylindrical probes. The next subsection describes the experimental apparatus and includes a description of the physical dimensions of the probe and the electrical connections as well as a description of the electronics and the software that collects the data. The following subsection describes the data reduction used to determine $V_f$ and $V_s$ using the single probe characteristic, and $T_e$ and $n_e$ using the double probe characteristic. Experimental complications of the these techniques will be discussed in the final subsection.
2.2.1.1 Experimental Arrangement of Langmuir Probe

The Langmuir probe used for these experiments consists of a 0.953 cm dia. pyrex tube, approximately 10 cm long, with two platinum electrodes encased in 1 mm pyrex sheaths, and uranium-doped glass as the sealing bead (Fig. 2.4). The probes protrude from the end of the tube with a probe-to-probe spacing of 7 mm. The actual electrode dimensions are 0.56 mm (24 gauge) dia. x 1.91 cm long. The 3 mm of the exposed probe leads adjacent to the glass seal are covered with an alumina insulator, 3 mm x 1 mm, to help prevent probe area growth by formation of conductive silicon layers on the pyrex body. The probes are mounted on the baseplate of the sample heater so that it is possible to position the probe tips anywhere along the axis of the chamber, from just inside the mouth of the plasma tube to the load lock. The electrical connections are made between stainless steel conductors of the vacuum feedthrough and probes with copper connectors in the space behind the baseplate. In order to minimize the influence of these biased and exposed contacts, they are covered with either a ground shield of aluminum foil or a specially fitted copper cylinder. The leads are joined to two external single strand copper wires that run

![Diagram](image-url)
the length of the 91 cm stainless steel feedthrough. The cabling is covered with coaxial ground shielding to minimize pickup since the feedthrough itself is electrically floating and may not provide adequate shielding. The probe is connected to the Keithley 236/237 source measurement unit using a triaxial connector. The low potential probe connection is either hooked up to the second probe for double probe measurements, or to the chamber for single probe measurements. The middle conductor of the triax cable, which is power supply driven shield, is connected to the ground shields of the coaxial piston cables.

The Keithley 236/237 voltage/current source measurement units are capable of acting as current and voltage sources in the voltage and current measuring modes, respectively. The electrical sources can be electrically isolated and can drive/detect ±110V at 100mA. The model 237 can also drive ±1100 V at 10 mA. The Keithley 237 samples at rates as high as 1000 samples/sec and is totally controllable via an IEEE-488 bus. This bus was connected to an IEEE-488 connector on a 33 MHz 80386 IBM-compatible computer via a doubly shielded 8 m IEEE-488 cable and functioned with no transmission faults. A Keithley 251 software application, coordinated the collection and triggering of the Keithley 237, and displayed the data. The program also displays the data so that the slopes and intercepts of the saturation curves and the zero voltage slope of the transition region can easily be determined.

2.2.1.2 Data Reduction

The single probe characteristic may be used to determine $V_s$ and $V_f$, as well as provide information about the EEDF. A schematic of a typical $I_e$-V characteristic for a single probe measurement is shown in Fig. 2.5. When the probe is held at a large positive voltage relative to the plasma it attracts negative particles and when biased at a large negative voltage it detects a positive current. It is assumed that all negative particles are electrons. There are three regions of the curve: the ion and electron saturation regions and the transition region. The transition region ($-V_f < V < V_s$) is where the electron and ion
Figure 2.5- Schematic I-V Characteristic of a Single Langmuir Probe.
-29-
current components are changing rapidly; the shape of the curve in the transition region is
governed by the EEDF. The floating potential, $V_f$, is the potential at which the + ion and
electron currents are the same. The space charge potential, $V_s$, is defined as the intercept of
the electron saturation portion of the curve. At $V_s$, the electric field between the probe and
the plasma is zero, so that the charged particles only reach the probe through thermal
diffusion. Electrons make up the dominant current component at $V_s$ because of their higher
velocity.

The double Langmuir probe utilizes a second conductor in contact with the plasma
so that a complete current path may be completed irrespective of the ground, thus
minimizing the disturbance of the plasma by the probe intrusion and allowing the electrodes
to follow the varying $E$ field for cases of rf plasmas. In afterglow plasmas such as the
downstream glow, this feature is quite important because charge generation away from the
main excitation is too low to make up for the charge drawn away by the probes. With no
applied voltage, the device of course draws no current. But when a voltage is present, there
will be a net flow of electrons due to + attraction and - repulsion. The opposite occurs with
the positive ions. The double probe characteristic has features similar to the single probe
curve, but the magnitude of the respective saturation curves is a function of the probe areas.
Therefore, data reduction can be simplified by using probes with identical dimensions.
Fig. 2.6 is an illustration of a symmetric double probe I-V characteristic.

$T_e$ may be found from an analysis of the double probe curve shown in Fig. 2.6.
The current produced by the applied potential is $-(I_{1+} - I_{1-}) + (I_{2+} - I_{2-}) = 2I$, where $I$
is the measured current and the - and the + signs represent the electron and ion current
components, respectively for probes 1 and 2. Using Kirchhoff’s law that states that the
current is the same at every point in the circuit, with the above mentioned detected current
equation, yields $I = I_{2+} - I_{2-} = I_{1+} - I_{1-}$. This equation is the definition of the current
measured for any point of the I-V curve. In the transition region of the curve, the current
can be shown as a function of the voltage. If a Maxwellian distribution of electrons is assumed, then

\[ I_{1-} = A_{1j_r} \exp \left( \frac{eV_1}{kT_e} \right) \]  \hspace{1cm} (2.14)

where \( A_1 \) is the area of probe 1, \( j_r \) is the random electron current density, and \( V_1 \) is the potential of probe 1, which is defined relative to probe 2 by \( V = V_1 - V_2 > 0 \). By using this equation with the constant current point rule, utilizing the probe definition, and having identical probe areas, the current relation for electrons is simply [2.3],

\[ \frac{I_+ + I}{I_+ - I} = \exp \left( \frac{eV}{kT_e} \right) \]  \hspace{1cm} (2.15)

where \( I_+ = I_{1+} + I_{2+} \). An alternative formulation gives another method of estimating \( T_e \) which is the voltage dependent first derivative of the current. By examining the dependence of current collection as a function of the applied potential, it is possible to set up the following equation,
\[ T_e = \frac{e}{k} \frac{I_{1+} I_{2+}}{I_{1+} + I_{2+}} \left( \frac{dI}{dV} \bigg|_0 \right)^{-1}. \]  

(2.16)

where the derivative is the slope of the I-V curve at \( V = 0 \) V.

Once \( T_e \) is determined it is possible to calculate the electron density. Langmuir's analysis assumed that the ion and electron kinetic energies are the same. However, when ions are lower average kinetic energy than electrons the Bohm, Burhop, Massey theory [2.7] yields an approximate equation for the saturation ion flux,

\[ I = \frac{1}{2} n A \left( \frac{kT_e}{M} \right)^{1/2}. \]  

(2.10)

where \( A \) is the probe surface area, \( M \) is the ion mass, and \( n \) is the charged particle density. This equation neglects the voltage dependence created by changing sheath characteristics and yields the electron density to within an order of magnitude. The greatest source of error using this equation is the change in sheath area with potential for a cylindrical probe. As the voltage difference between the probe and plasma increases, the sheath area will also increase thus providing greater current at the probe.

2.2.1.3 Experimental Limitations

The data collected using the Langmuir probe provides information about the electron temperature and the charged particle density in different positions of the chamber. However, care must be taken when interpreting the results of the data derived through standard analysis techniques. The most important limitation is that the calculations assume that the EEDF is Maxwellian, which is true only when dominated by electron-electron collisions. Moisan et al. have shown that for low frequency discharges there is a high electron energy tail, which diminishes as the electron-neutral collision frequency, \( v \), plasma frequency, \( \omega \), ratio \( (v/\omega) \) decreases towards 0. [2.4,2.5] Figure 1.1 shows a plot of the density of states as a function of electron energy for different \( v/\omega \) values. The high energy tail shown in Fig. 1.1 for the high \( v/\omega \) value discharges, leads to artificially high \( <T_e> \)
estimates. Therefore, $T_e$ as calculated from Langmuir probe data stated in this thesis is actually an effective electron temperature for a non-Maxwellian EEDF.

The primary experimental limitation that leads to inaccuracies of the probe data collected is the construction of the circuit itself. The probe is simply two wires that run directly to an isolated current measuring circuit. For a dc discharge this arrangement would be adequate, but since the discharges have a time varying potential, the probes "lag and lead" because the probes do not have impedance matching to tune them to the plasma impedance. The potential fluctuations will change the sheath radius during the cycle, a phenomenon which is not easily modeled, and hence not normally included in most probe analyses. Therefore, without the matching network the actual electron density differs from the estimated electron density, especially for collisionless sheath approximations [2,6,2.7].

Introduction of a single probe into the plasma can provide a large external bias. Therefore, care must be taken when analyzing the single probe characteristic. The large bias may actually create a second glow region, especially if the collisional mean free path is substantially less than the sheath distance.

2.2.2 Mass Spectrometry

This subsection describes the construction and uses of the quadrupole mass spectrometer. The first part will describe the function of the components of the C50 mass spectrometer system and the theory of the quadrupole filter operation. The second part will describe the experiments that are performed with the instrument: mass scanning and energy scanning experiments. Finally, the third part will discuss limitations of mass spectrometry.

2.2.2.1 Quadrupole Mass Spectrometer Construction

The quadrupole mass spectrometer is an EXTREL model C50 and is housed in a custom-built 10.2 cm diameter stainless steel chamber with dedicated backing pumps, a Leybold TMP360V turbomolecular pump and a Leybold D4B rotary vane backing pump. The ionizer of the mass spectrometer lies within one flange of a 6 in. gate valve. The
sniffer tube is 1.6 cm in diameter and 8.9 cm long and ends in a 150 μm orifice which admits gas from the reactor. The sniffer tube is mounted directly to the other gate valve flange and to a 2 1/8 in. diameter flange attached to a welded bellows. When the sniffer is fully inserted it lies about 3.8 cm from the reactor axis. The distance between the sniffer tube orifice and the ionizer is 7.62 cm.

In the remote data collection mode, the mass spectrometer is controlled by using an IBM-AT clone via a Data Translation 2800 data acquisition board. It can also be operated in a manual mode for RGA applications. The software that controls the spectrometer is an ASYST-based application called MASPECK (see Appendix 11.1 for the source code of version 56). This program can be used to control the mass and the ionizer electron energy, so the mass spectrometer can perform both the mass scanning and energy scanning experiments. The program has the ability to display and plot multiple files under normal or magnified viewing modes. In addition, it can be used to identify for peak intensities and save the output as ASCII files for use by IBM or Macintosh applications.

The three major components of the mass spectrometer are: 1) an ionization/ion focusing system, 2) a quadrupole mass separation filter, and 3) a multiplier tube signal amplifier and detector system (Fig. 2.7.) The ion generator is at the entrance of the mass spectrometer and uses a tungsten filament that is negatively biased with respect to an electron collection cage (usually 70 V.) Electrons are accelerated towards the center of the electron collection cage where they collide with molecular species inside the cage causing fragmentation and ionization. The ion beam passes through a series of electrostatic lenses to collimate the beam. Once focused, the beam then passes a biasing plate into the quadrupole filter. The biasing plate acts as a physical shield against off-axis particles and as an electrical shield against E fields which minimizes the effect of the quadrupole filter fields on the ion optics.
Figure 2.7- Schematic Diagram of a Quadrupole Filtered Mass Spectrometer.
The quadrupole filter consists of four 3/8 in. dia. cylinders that are on axis with the incoming beam. The poles are wired such that opposite poles are connected with one pair bearing a positive dc bias and applied rf signal and the other pair bearing an electrical potential with the opposite sign. The potential function of the applied electric field is [2.8]

$$\phi = (V_1 + V_0 \cos \omega t) \frac{x^2 - y^2}{r_0^2}.$$  \hspace{1cm} (2.1)

where $\phi$ is the potential function, $V_1$ and $V_0$ are dc and ac voltage amplitudes, $x$ and $y$ are the $x$ and $y$ axes, and $r_0$ is the radius circumscribed by the poles. Equation (2.1) assumes the poles are perfectly hyperbolic conducting surfaces. Since there is no acceleration in the $z$-axis (the axis parallel to the poles), the filter does not alter the axial velocity of charged particles. The equations of motion for the pole directions are therefore,

$$m \ddot{x} + \frac{2e}{r_0^2} (V_1 + V_0 \cos \omega t) x = 0 \hspace{1cm} (2.5)$$

$$m \ddot{y} - \frac{2e}{r_0^2} (V_1 + V_0 \cos \omega t) y = 0 \hspace{1cm} (2.6)$$

$$m \ddot{z} = 0. \hspace{1cm} (2.7)$$

For a given set of voltage amplitudes and frequencies there will be many masses with unstable trajectories, but only one mass-to-charge ratio ($m/z$) range with a stable trajectory. An unstable trajectory is one that removes the particle from the filter axis [2.9]. The stability diagram is a plot of non-dimensional parameters $(8\theta V_1)/{(\omega^2 m r_0^2)}$ and $(4\theta V_0)/{(\omega^2 m r_0^2)}$ that shows whether or not a particular $m/z$ will have a stable trajectory through the filter (Fig. 2.8). If the plotted point falls outside of the triangular region the trajectory will be unstable, hence the particle is rejected. By appropriate choices of applied voltage, it is possible to tune the filter to pass very narrow $m/z$ ranges.

The mass resolution of the 3/8 in. Extrel C50 quadrupole is defined by [2.10],

$$\frac{m}{\Delta m} = \frac{0.126}{0.16784 - V_1/V_2} \hspace{1cm} (2.7)$$

where, \hspace{1cm} $V_1 = 0.193 \frac{m \omega^2 r_0^2}{1.149 \frac{m \omega^2 r_0^2}}$. 

Figure 2.8- Stability diagram plot of quadrupole mass filter [2.9].

In order to achieve theoretically infinite resolution, the ratio of $V_1/V_2$ would have to be 0.16784, which can also be written by $V_1 = \gamma V_2$, or $\gamma = 0.16784$ [2.10]. When $\gamma$ exceeds 0.16784, the filter throughput starts to decline without improvement in real resolution. In actual operation of the mass spectrometer, the mass control circuitry applies $V_1$ and $V_2$ as functions of $\gamma$ and $\delta$, where $V_1 = \gamma V_2 - \delta$, and $\delta$, pole bias potential. When $\delta=0$, the mass resolution is mass independent. The $\Delta m$ knob on the mass spectrometer controls the $\gamma$ amplification while the $\Delta m$ knob controls the $\delta$ bias.

The detection system consists of a dynode plate and a channeltron electron amplifier tube. Charged particles that pass through the axis of the quadrupole filter unperturbed, enter the detector. The dynode is biased to a high potential with the charge opposite of the species being detected (~2 to 4 kV.) The ions accelerate towards the dynode where they
liberate a cloud of electrons upon impact. The cloud of secondary electrons are repelled by
the dynode and are pushed towards the relatively less-biased channeltron (~0.8 to
-1.7 kV.) The surface of the channeltron is a continuous dynode electron multiplier,
amplifying the electron cloud through emitted electron cascades.

2.2.2.2 Experimental Techniques

There are three types of mass scan experiments that can be performed sampling
species from a plasma. All of the techniques have at least one ionization source, either the
ionizer of the mass spectrometer or the plasma. The first method involves simply turning
off the ionizer and drawing ions from the plasma. Since only externally generated ions are
detected, the peak heights are indicative of the relative ion abundance in the reactor. The
second method involves using the mass spectrometer ionizer and the plasma in tandem to
monitor all species produced in the chamber. The additional ionization source provides a
signal from the neutrals passing through the spectrometer. However, the ionizer off signal
cannot be subtracted from the ionizer on signal to determine the portion of the signal caused
by neutral species. The ionizer will further ionize and fragment polyatomic ions. This
technique is good for general mass scans because it shows the neutral fragmentation
concentration when the ion concentration is low. The third method uses the ionizer as the
sole ionization source. By placing a magnet adjacent to the throat of the sniffer tube, it is
possible to deflect the ions into the sniffer tube walls so that they do not enter the mass
spectrometer. Therefore, it is possible to detect only neutral species with this technique.

The energy scan experiment is used to detect the presence of metastable species and
is also known as an appearance potential measurement. This experiment monitors the
signal of a single m/z as the electron beam energy of the ionizer is ramped. As soon as the
electron beam acquires enough energy to ionize a specific molecular fragment, the signal
increases. The spectrum is essentially an integrated intensity for excitation of the measured
m/z with respect to the electron beam energy. If metastable species are present, a signal
will appear at the energy equivalent to the difference between ionization energy and the species initial energy state. By differentiating the integrated spectrum, the energy positions are revealed making it possible to identify the presence of metastable species. When this experiment is performed under carefully controlled conditions, it can be used to determine the electron impact ionization cross-section.

2.2.2.3 Experimental Limitations

There are several practical limitations which must be considered when interpreting mass spectrometer data. Because the technique is not a direct measurement of neutral species, it is important to remember that the data is a fingerprint of the parent species. In addition, the mass spectrometer does not have uniform sensitivity at every m/z, so it is generally not possible to make direct comparisons between intensities of different m/z peaks. Finally, the spectrometer itself is prone to some drift in its settings. This subsection will describe the sources of these limitations and procedures to minimize their effect.

When interpreting mass spectrometer data while using an internal ionization source, the signal is not directly representative of the species entering the mass spectrometer chamber, but rather products of the fragmentation. Therefore, a cracking pattern is necessary to determine the partial pressure of the gas detected. A cracking pattern plot is simply a graph showing the relationship between various daughter-species m/z ratios and the partial pressure of the parent species. By using a m/z peak that is known to belong to only one parent species, it is possible to use the peak ratios of the cracking pattern to remove the contribution of that parent from the other peaks. If the cracking pattern is not known for a species, changes in the peak height can indicate relative changes in the partial pressure of that compound, but cannot relate the relative abundance of that parent species to other compounds.

The sensitivity of the mass spectrometer to ions depends on several factors. The ionizer electron optics focus the ions onto the axis of the quadrupole, but since the ions
have different masses, the focusing is not uniform. This can lead to chomic-aberration-like errors in transmission through the lenses. Another consideration is that the secondary electron emission coefficient of the conversion dynode is dependent on the mass of the bombarding particle. Helium will have a lower conversion efficiency than iron or silicon, thus reducing the sensitivity of the detector to helium. A third consideration arises because the poles are of a finite length. The fields near the ends of the filter alter the throughput of the filter. Recent quadrupole filter designs minimize this effect by using short quadrupoles at either end which are biased with only the ac potential. The Exrel C50 unit does not have such end quadrupoles.

The mass spectrometer has many operations which affect the output signal. Some parameters, such as channeltron voltage and preamplifier gain, affect the intensity of the entire mass range uniformly. However, factors such as the surface state of the detector and power supply drift can change the signal amplification. In order to accommodate these factors, two procedures are employed to allow comparison of data. The first procedure requires recording the mass spectrometer settings. As long as the settings remain within predetermined ranges the machine is not considered to have drifted. Once the settings are optimized, they are not changed until the series of related experiments is completed. This provides a degree of reproducibility by assuring that mass-dependent factors remain as constant as possible. The second procedure involves periodic collection of spectra under known conditions and normalization of data collected before and after such a scan.

2.2.3 Optical Emission Spectroscopy

Optical emission spectroscopy (OES) analyzes visible radiation from the plasma. The primary use of this technique is to monitor spectral lines and relating them to changes in the population of excited species as a function of changes in experimental parameters. However, since many excited states do not decay radiatively or have long lifetimes, the
technique does not detect all species. In this thesis, OES data is presented to show the dependence of certain excited states upon changes in added gases, and plasma power.

The optical emission unit used is a Tracor-Northern TN6500 unit. It consists of a Polymicro Technologies 1148 fiber optic light pipe that transmits the signal from the Pyrex chamber window to the 0.5 m Czerny-Turner monochromator. There the light passes through a 25 μm wide slit, is reflected by one of three gratings (150, 300 and 600 l/mm gratings) and onto a 1024 light-intensified photodiode array (of which only about 700 diodes are used.) The signal is then passed onto a IBM PC-based Tracor-Northern computer unit which is used to display and save the data. The power supply unit also provides control to the intensifier bias so that a wide range of light signal levels may be detected by the diodes. The data is down-loaded to an IBM-AT 386-based computer with an ASYST-based application via a RS423-RS232 datalink. From there, the ASYST application OESPECT determines peak intensities, transfers the intensity data to an ASCII file, and is used to plot the raw data.

2.2.4 Ex-situ Techniques
2.2.4.1 Infrared Spectroscopy

Because the energy required for motion of atoms within molecules is the same as the energy of infrared photons, infrared spectroscopy, ir, can be used to provide information about many aspects of the local atomic structure of certain solids. In this thesis, ir is used to determine the hydrogen content in films, the average bond angle of amorphous network Si-O-Si bonds, and the local bonding environments of hydrogen-terminated molecular groups. This subsection will describe the equipment used for making the measurements, how the data is converted into a useful form, and how the data is used to characterize the films measured.

Infrared measurements of the films were made using a Perkin-Elmer 983 spectrophotometer operating in a double beam optical transmission mode. While the
PE983 is a stand-alone instrument, it is normally controlled by a computer to facilitate data analysis. The atmosphere of the PE983 is recirculated through a CD3 Air Dryer which has a regenerating zeolite core to remove water vapor. The spectrophotometer uses a glow-bar light source which emits a continuum infrared spectrum and uses a double beam optical path to measure transmission. The beam is split by a chopper that sends the light on two separate paths through the sample region. One path contains only sample atmosphere while the other contains the thin film sample and substrate mounted perpendicular to the beam. The two beams of light are recombined into a single light path by another chopper and mirror, and are diffracted and filtered by the monochromator. The substrate used for these measurements is typically a high resistivity crystalline Si substrate (≈10-100 Ω-cm) which is highly transparent to infrared radiation in the range of 5000 to 200 cm⁻¹. The high resistivity material is required to minimize the free carrier absorption and provides an average transmission of about 55%, except for a dissolved oxygen band O-Si(s) at ≈1100 cm⁻¹ and a strong multiple phonon absorption band at ≈610 cm⁻¹. An initial scan of the bare substrate is made before deposition so that these features may be eliminated from the final spectrum.

The infrared spectrometer collects the data as transmittance, but it must be converted to absorbance to be used for quantitative determinations such as estimating the hydrogen concentration of the films. The following derivation briefly shows how transmittance data is converted into absorbance data, then shows how the absorption coefficient is determined. Absorbance is defined as,

\[ A \equiv \log_{10}(T/T_0) \]  
(2.20)

where \( T_0 \) is the reference transmittance and \( T \) is the transmittance of the film and substrate.

The two loss mechanisms, reflectance and absorbance, may be combined to provide a function of the actual transmittance. Consider that when light transverses the medium, a fraction of it is absorbed \((e^{-\alpha t})\), where \( \alpha \) is the absorption coefficient and \( t \) is the thickness
of the thin film. By summing the fractional loss term in the multiple reflection term, the transmittance is modified into,

\[ T = \frac{(1-R)^2}{(1 - R^2 \exp^{-2\alpha t})} \exp^{-\alpha t} \]  

(2.21)

where R is reflectance. The \( \exp^{-2\alpha t} \) term accounts for absorption due to multiple internal reflections: it may be neglected for small \( \alpha t \), (\( \exp^{-2\alpha t} \to 1 \)), so that the transmittance reduces to,

\[ T = \frac{1 - R}{1 + R} \exp^{-\alpha t} = T_0 \exp^{-\alpha t}. \]  

(2.22)

The baseline transmittance, \( T_0 \), which in this case is the substrate with all of its loss mechanisms, is equivalent to the reflectance function in the case of thin films, therefore transmittance is a function of \( \alpha \). Therefore, the absorption coefficient can be defined as,

\[ \alpha = -\frac{1}{t} \exp\frac{T}{T_0}. \]  

(2.23)

By substituting in equation (2.22) into equation (2.20), the equation for experimentally determining the absorption coefficient is,

\[ \alpha = 2.3025 \frac{A}{t} \]  

(2.24)

The absorbance depends upon the photon energy since the molecular vibrational modes occur only at certain energies which are governed by the oscillator strengths and atomic masses. Hence, both \( \alpha \) and \( A \) are strong functions of the photon frequency, \( \omega \).

2.2.4.1.1 Compositional measurements

Infrared spectroscopy is used to quantify the concentration of the major constituents of suitably transparent thin films. By establishing the concentration of a given component through independently verifiable means, it is possible to find a proportionality function that is dependent on \( \alpha \) and \( \omega \). For example, Fang et al. used a neutron activated \( \gamma \)-ray producing nuclear reaction to determine the hydrogen concentration of Si films and then compared the integrated intensities of the SiH stretching (s) 2000 cm\(^{-1}\) and SiH wagging
The relationship between bond concentration and integrated intensity is,

\[ N_H = K' \int_{\omega_0}^{\omega} \frac{\alpha(\omega)}{\omega} \, d\omega \quad \text{or} \quad N_H = K \int_{\omega_0}^{\omega} \alpha(\omega) \, d\omega \quad (2.25) \]

where \( N \) is the bond concentration (\( N_H \) is the bonded hydrogen concentration), \( K' \) and \( K \) are the empirically determined oscillator strength constants, and \( \omega_0 \) is the excitation frequency. Since, the absorption coefficient is being applied to a single frequency, \( \omega \) is considered constant and hence removed from the integral; the empirical constant \( K \) is approximately related to \( K' \) by \( K = K'/\omega \). Therefore the number of bonds is simply a function of the area under the absorption peak. These equations are often approximated by \( N_H = K_0 \alpha H \), where \( H \) is the full width half maximum (FHWM) of the absorbance band. The final equation is,

\[ N_H = K_H 2.3025 \frac{\Delta A}{t} \quad (2.26) \]

\( N_H \) calculated by equation (2.26) is the concentration of bonds in the material; therefore, the total number of bonds must be known in order to provide the actual concentration. Since hydrogen forms only one bond, the bond concentration is also the bonded hydrogen concentration. A number of values compiled by Adams for the constant \( K \) for different hydrogen bonding groups are listed in Table 2.1: [2.12]

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>( K ) (10(^{16}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>Si(_3)N(_4)</td>
<td>a-Si:H</td>
</tr>
<tr>
<td>OH(s)</td>
<td>3620</td>
<td></td>
</tr>
<tr>
<td>OH(s)</td>
<td>3380</td>
<td></td>
</tr>
<tr>
<td>NH(s)</td>
<td>3340</td>
<td></td>
</tr>
<tr>
<td>SiH(s)</td>
<td>2270, 2170</td>
<td>2000</td>
</tr>
<tr>
<td>SiH(w)</td>
<td>630</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2.1- Hydrogen concentration absorption constants.
-45-

dipole moments, then their resonant vibrational frequency will be modified. Purely theoretical treatments of the modification are extremely complicated because of 1) the potential function of the A-H group, 2) other vibrations in the A-H...B system, and 3) local environment [2.18]. Lippincott et al. first predicted the relationship between the dipole bond length and the mean frequency of the A-H stretching vibration [2.19]. Figure 2.9 shows the relationship between the mean vibrational frequency of OH(s) frequency and O--O distance [2.20]. As the distance between neighboring hydroxyl groups decreases, the resonance energy of the stretching mode also decreases due to an effective lowering of the O-H stretching force constant. The data is a collection of x-ray diffraction data of organic crystals, in which the OH(s) vibrational bond length can be determined. Figure 2.10 shows a similar relationship between the NH(s) frequency and N--N bond length [2.20].

2.2.4.2 Transmission Electron Microscopy

The transmission electron microscope (TEM) technique is used in an imaging mode, in which a highly focused electron beam penetrates a thinned sample to form an image on a phosphor screen [2.22]. Ordered regions of the sample (crystals) will interact with the beam to create an image related to the lattice. This technique enables examination of crystal orientation, and clearly shows defects within the crystals. The transmission electron microscope used in these studies was a HRTEM, JEOL 200CX, and was used to image the epitaxial silicon films described in Chapter 6.

2.2.4.3 High Resolution Scanning Electron Microscopy

The high resolution scanning electron microscopy technique (HRSEM) uses a focused electron beam to illuminate a sample by rastering the beam across its surface. Secondary electrons radiating from the sample are used as the signal source. The image is created by coordinating the timing between the rastering electron beam in the microscope
Figure 2.9- Relation between OH stretching frequency and O···O distance [2.20].

Figure 2.10- Relation between NH stretching frequency and N···N distance [2.20].
References


3 Plasma Behavior

In order to understand the reactions that occur in any CVD system, it is necessary to characterize the behavior of the excitation source. For plasma-driven techniques, charged species produced by the plasma are known to be directly involved in certain deposition reactions such as a-Si:H deposition, and indirectly responsible for others [3.1-3.5]. It has also been shown that the additions of other compounds to the inert gas discharge may change the electrical properties of the plasma. Therefore the purpose of this chapter is to show the concentration and energy of electrons in the reactor under conditions similar to those for deposition.

3.1 Objectives

To demonstrate the charge concentration and electron energy behavior in the reactor, these two parameters are examined as functions of excitation frequency, power, and additional gases. These parameters determine the behavior of the discharge and the electrically charged species derived from them. Excitation frequency and power application geometry can affect the mode of power coupling with the plasma and to a large extent determine the EEDF for the majority of electrons. For the experimental conditions used, the applied power controls the concentration of excited states, hence it governs the maximum reaction rates. The addition of other gases such as NH₃ to the discharge can produce other excited species and provide other channels for energy storage.

3.2 Approach

The double Langmuir probe technique is used to determine the effective electron temperature and electron density of the plasma afterglow. The single Langmuir probe is used to determine the plasma self-bias and space charge potential. Measurements were made by moving the Langmuir probe to a given position, then taking the appropriate measurements at specified power levels. It should be noted that the probe position is defined as the base of the Langmuir probe tips.
The default conditions used for the experiments discussed in this chapter include pure He discharges, 200 sccm total gas flow through the plasma tube, and a pressure of 300 mTorr. No SiH₄ was injected into the chamber during measurements to prevent probe contamination. For the frequency effect measurements the power was maintained at 25W for 13.56 MHz, and 170W for 2.54 GHz. The high microwave power level was required to maintain the 2.54 GHz discharge within the waveguide applicator due to difficulties in impedance matching caused by the inserted coaxial cable and the high ionization potential of the He feedstock gas.

3.3 Results

3.3.1 Effect of Position

Figure 3.1 shows how $T_e$ changes with respect to distance from the plasma tube for different plasma powers at 13.56 MHz. The data points were collected as a function of power; and the Langmuir probe position was changed after each set of power measurements. For each series, the behavior with respect to position is the same. $T_e$ decreases from the mouth of the plasma tube to a minimum about 8.5 cm downstream, then reaches a maxima at 15 cm, where the probe tips are in the vicinity of the first gas dispersal ring. The 10W curve shows a steep drop between 15 and 19 cm, however it should be noted that for these curves the transition region of the characteristic is relatively small, (less than 100 pA/V, and fewer than 5 data points are available for calculating $T_e$).

Figure 3.2 shows $n_e$ plotted logarithmically as a function of probe position within the chamber for all power levels. As the power decreases from 100W to 10W, $n_e$ decreases one order of magnitude at the plasma tube opening, at 13.5 cm the corresponding change is about 1.8 orders of magnitude, and at 40 cm it is 2.5 orders of magnitude. At the lowest power levels 10 and 30W, $n_e$ decreases approximately logarithmically as a function of distance. However, at higher power levels, a region of constant electron density around 15 cm downstream appears.
Figure 3.1- Plot of Te as a function of probe distance from the end of the plasma tube at 13.56 MHz. 300 mTorr, 200 sccm He, 10, 30, 50, 75, and 100 W.
3.3.2 Effect of Frequency

Figure 3.3 shows the electron density with respect to distance from the opening of the plasma tube for 25 W at 13.56 MHz, and 170 W at 2.54 GHz. At the plasma tube opening, the electron density, \( n_e \), for the 13.56 MHz discharge is roughly 2.5 orders of magnitude greater than that of the 2.54 GHz discharge, even though the applied power level is almost 7 times greater for the 2.54 GHz discharge. The decrease in \( n_e \) moving away from the plasma tube opening is approximately logarithmic. The 13.56 MHz \( n_e \) decreases by 4 orders of magnitude, and the 2.54 GHz density decreases by \( \sim 2.5 \) orders of magnitude at the far end of the chamber.

Electron temperature as a function of position is shown in Fig. 3.4 and range from 3.4 to 4.9 eV for the 13.56 MHz discharge, and from 3.0 to 1.5 eV for the 2.54 GHz discharge. The \( T_e \) for the 2.54 GHz discharge is about 30% lower than for the 13.56 MHz discharge at the mouth of the plasma tube. \( T_e \) for the 2.54 GHz discharge decreases linearly with respect to distance; i.e., there is no increase in \( T_e \) near the first set of gas dispersal rings as detected for 13.56 MHz discharges.

3.3.3 Effect of Power

Figure 3.5 shows \( T_e \) as a function of power, for positions 0 to 15 cm in 3.5a, and positions 19 to 34 cm in Figure 3.5b. The curves show two types of behavior, 1) a monotonic decrease or increase, and 2) a maxima at 30 to 40W with a steep decrease towards lower power and a gradual decrease towards higher power for curves of positions greater than 15 cm. The curves that have the maxima near 40W are from positions near the plasma tube or just downstream of the gas dispersal ring. In addition, the curves corresponding to positions near the minima of the curves in Fig. 3.1 show smaller fluctuations in \( T_e \), 0.25 eV, than those curves near the \( T_e \) maxima, of 0.85 eV.

Figure 3.6 shows the \( n_e \) as a function of power for each probe position. Figure 3.6a shows that the \( n_e \) dependence follows a sub-linear power function for positions less than 13.5 cm from the gas dispersal ring position, while positions greater than 13.5 cm
Figure 3.3- Plot of $n_e$ as a function of position for 13.56 MHz and 2.54 GHz excitation frequencies. 200 sccm He, 300 mTorr, 25W at 13.56 MHz and 170W at 2.54 GHz.
Figure 3.4- Plot of Te as a function of position for 13.56 MHz and 2.54 GHz excitation frequencies. 200 sccm He, 300 mTorr, 25W at 13.56 MHz and 170W at 2.54 GHz.
Figure 3.5- Plot of $T_e$ as a function of power at 13.56 MHz. 300 mTorr, 200 sccm He. a) 0, 3.81, 7.62, 11.43, and 15.24 cm downstream, b) 19.05, 26.67, and 34.3 cm downstream.
show a super-linear dependence, as seen in Figure 3.6b. Fig. 3.6 also shows that as the probe moves further from the plasma tube, the exponent of the curve equation increases.

3.3.4 Effect of Gas Composition

Figures 3.7 and 3.8 show the effect of the N-atom source gas concentration on $T_e$ and $n_e$ of 13.56 MHz and 2.54 GHz discharges, respectively. The probe is positioned at the mouth of the plasma tube. Figure 3.7a shows no change in $T_e$ as a function of flow rate for either N$_2$ or NH$_3$ at 13.56 MHz. $T_e$ ranges from 2.6 to 5.5 eV. The $n_e$ (Fig. 3.7b) shows a logarithmic decrease for both gases with the rate of decrease slightly larger for N$_2$, but the total change is less than one order of magnitude. The 2.54 GHz $T_e$ is lower than $T_e$ for 13.56 MHz discharges, but $T_e$ shows a decline above 50 sccm of the N-atom source gas for the 2.54 GHz discharge. Electron density remains within an order of magnitude across the entire range of flow rates. While the N$_2$ curve shows a slight downward trend, the NH$_3$ curve shows an initial drop, reaching a minima about 20 sccm NH$_3$, then gradually increasing and leveling off by 100 sccm. The overall electron density is 2.5 orders of magnitude lower for 2.54 GHz discharges than for 13.56 MHz discharges.

3.3.5 Single Langmuir Probe Characteristic

The single probe I-V plot provides information about the floating potential of the plasma. Figure 3.9 shows the probe characteristic of a single probe measurement for 13.56 MHz, 75W, 300 mTorr, at 3, 13, and 39 cm downstream from the plasma tube [3.6]. Figure 3.10 shows the probe characteristics for the same positions as the 13.56 MHz probe positions for a 2.54 GHz, 170W, 300 mTorr discharge. The plasma floating potential is the point on the I-V curve of zero current. For both the rf and microwave discharges, the floating potential becomes increasingly positive as the probe distance from the plasma tube increases. For both frequencies at 39 cm from the plasma tube, the floating potential is between 65 and 70 V, and the space charge potential at 3 cm downstream from the 13.56 MHz discharge is 32 V.
Figure 3.6- Plot of $n_e$ as a function of power at 13.56 MHz. 300 mTorr, 200 sccm He, a) 0, 3.81 and 7.62 cm downstream, b) 19.05, 26.67, and 34.3 cm downstream.
Figure 3.7 - $T_e$ as a function of N source gas flow rate. a) 13.56 MHz, 25W, b) 2.54 GHz, 170W.
Figure 3.8- $n_e$ as a function of N source gas flow rate. a) 13.56 MHz, 25W, b) 2.54 GHz, 170W.
Figure 3.9- Single Langmuir Probe I-V curves for 13.56 MHz He discharge at 300 mTorr. Sampling positions 3, 13, and 39 cm downstream.
plasma, an electrodeless discharge created in a glass envelope, \( n_e \) is significantly higher for 2.54 GHz than for 13.56 MHz discharges [3.7,3.8,3.11]. The difference in \( n_e \) in the excitation region is not maintained in the chamber, because the electric field extends beyond the plasma excitation region. It is a direct result of the different electrode configurations and discharge excitation frequencies used for initiating and maintaining the plasma discharge [3.4]. Figure 3.3 shows that the 2.54 GHz discharge does not have the same degree of charge transport into the chamber, demonstrating that electric fields extending into the chamber are reduced. For the 2.54 GHz discharge, charge can only be transported into the chamber by thermal diffusion and gas flow. Thus it can be concluded that electrons are more likely to play a role in deposition reactions for the 13.56 MHz excitation than for the 2.54 GHz excitation, simply because of the electrode structures and excitation frequencies used to sustain the plasmas.

The similarity of the absolute value of \( T_e \) for both 2.54 GHz and 13.56 MHz discharges is somewhat puzzling. It would be expected that the microwave \( T_e \) be almost an order of magnitude lower [3.12] One explanation is that a high energy tail of electrons exists in the discharge due to He Penning ionization reactions. Such reactions emit electrons with high energy compared with the bulk energy, 15-20 eV, vs. 0.1-2 eV. The rate constant for Penning self-ionization is [3.13],

\[
\text{He}^* + \text{He}^* \rightarrow \text{He} + \text{He}^+ + e^- \quad <\sigma v_e> = 2.7 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}. \quad (3.7)
\]

High energy electrons shift \( T_e \) estimates of Langmuir probe data to artificially high values.

### 3.4.3 Effect of Power on the Plasma

The behavior of the electron density as a function of power changes with respect to distance, and is based on two independent phenomena, 1) charge generation due to Penning ionizations listed in equation (5.7), and 2) charge generation as a function of the power change. The shape of the curves shown in Fig. 3.6b shows the same behavior that is seen with light emission as a function of power. The light emission originates from the electron decay of electrically neutral species such as He*. Since the behavior of light
plasma tube opening, while Penning ionizations dominate at positions further away. The decrease in electron density as a function of other gases shows that energy is being stored in excited electrons and molecular vibrational and rotational modes.

References


4 Hydrogenated Amorphous Silicon Growth

The primary issue discussed in this chapter is how SiH$_4$ is consumed in the reactor. Since SiH$_4$ is the source of silicon in most of the reaction systems studied for remote PECVD deposition of Si-based thin films, a clear picture of the SiH$_4$ consumption paths is necessary. This chapter shows that exhausted SiH$_4$ and silicon film growth are not the only consumption channels for SiH$_4$, and that other channels such as gas phase polymerization and non-conversion can affect film growth.

4.1 Objectives

The objective of the experiments is to demonstrate the relationships between electron density and energy, and structural morphology of the films. The questions considered in this chapter deal with issues concerning SiH$_4$ interactions with a He discharge afterglow. First, the plasma species that contribute to silane excitation are considered. Then, the gaseous products of silane excitation are considered. Third, the deposition reaction order with respect to the initial reactants is revealed. Finally, the issues surrounding a-Si:H film precursor determination are discussed.

4.2 Approach

In order to identify the SiH$_4$ excitation mechanisms, mass spectrometry is used to show the gaseous products of plasma and electron impact excitation of SiH$_4$. Optical emission spectroscopy is used to show how the He afterglow is affected by the addition of SiH$_4$. Mass spectrometry is used to explore the gaseous products of plasma excitation of SiH$_4$. Using Langmuir probe and deposition rate data, it is possible to investigate the reaction order of the overall a-Si:H deposition.

The chamber operating pressure was maintained at 300 mTorr, the flow rates were 200 sccm He in the plasma tube, and 10 sccm 10% SiH$_4$ + He injected downstream through the gas dispersal ring. A 13.56 MHz power supply was used with the coil
applicator and a default power of 50W. The substrates for Raman samples were fused silica, while the ir samples used on high resistivity p-type Si. All samples were grown at 250°C.

4.3 Results

Optical emission spectroscopy was used to analyze changes in the spectral intensity of key lines from the plasma afterglow upon the addition of SiH₄. The second results subsection demonstrates the steady state concentration of SiH₄ in the chamber as a function of power and distance from the end of the plasma tube. The third section examines the formation of high molecular weight Si species as detected by ion concentration as a function of power, and SiH₄ flow rate. The fourth section shows how the a-Si:H deposition rate is dependent upon the electron density, and the SiH₄ concentration in the vicinity of the growing film. Finally, the manner in which Si-H groups in these films relate to deposition conditions is explored.

4.3.1 Optical Emission Spectroscopy

Figure 4.1 shows the normalized intensities of the 6561Å (3²D-2²p⁰ of H) and 4142Å (A²Δ-X²Π of SiH) lines with respect to the SiH₄ source gas flow rate [4.1,4.2]. These measurements were made in the reactor 2.54 cm downstream from the plasma tube. The two line intensities track each other at all flow rates. The signal intensities reach background levels above 10 sccm 10% SiH₄ and He in the downstream gas flow. Figure 4.2 shows the intensity of the 5876Å (3³D-2³P) and 5015Å (3¹P-2¹S) line intensities as a function of SiH₄ source gas flow rate [4.2,4.3]. The 5876Å intensity decreases from 10⁵ to 6000 cps, a 17 fold drop, while the 5015Å line decreases from 20500 to 2500 cps, an 8 fold drop. The ratio of 5876Å/5015Å declines from 5 to 2.5 for 0 sccm and 25 sccm SiH₄ respectively.
Figure 4.1- a) 4142Å and 6561Å optical emission spectroscopy signals as a function of 10% SiH₄ + He flow rate injected downstream. b) Normalized Intensity. 13.56 MHz discharge, 200 sccm He in the plasma tube, 300 mTorr, 50W, sampling from the first viewport, intensifier gain 6.0, 0.1 s sampling time, 1000 cycles.
Figure 4.2 - 5015Å and 5875Å optical emission spectroscopy signals as a function of 10% $\text{SiH}_4 + \text{He}$ flow rate injected downstream. 13.56 MHz discharge, 200 sccm He in the plasma tube, 300 mTorr, 50W, sampling from the first viewport, intensifier gain 6.0, 0.1 s sampling time, 1000 cycles.
4.3.2 High Molecular Weight Gas Phase Species

Figure 4.3a-c are mass spectrometer plots of ions between 20 and 320 m/z (Fig. 4.3a m/z 20-120, Fig. 4.3b m/z 120-240, and Fig. 4.3c m/z 240-360). The mass spectrometer is tuned to provide constant mass resolution and sensitivity throughout the mass range, and the intensities are normalized with respect to mass 31. The chamber conditions are 300 mTorr pressure, 200 sccm He plasma feedstock gas, 10 sccm 10% SiH₄ and He, and 50W power. Peak groups corresponding to SiₙHₓ (n=1) starting at mass 28 m/z to peak groups at 308 m/z (n=11) are spaced at about 28 m/z intervals, where n is the number of Si atoms in the cluster. Under higher power conditions it is possible to detect peak groups up to 336 m/z (n=12). The average peak intensity declines as the number of silicon atoms in each peak group increase. One exception is the peak group at 168 m/z, which tends to be 33-50% larger than the next lighter peak group at 140 m/z. For peak groups where n ranges from 2 to 4, the number of peaks present is equal to 2n + 4, one peak extra than a normal silicon alkane analog chain number of 2n + 3 mass peaks.

Figure 4.4 shows the effect of plasma power upon the relative peak heights within each cluster peak group for m/z 25-95 in Fig. 4.4a and m/z 105-175 in Fig. 4.4b. The conditions are 200 sccm He plasma feedstock, and 10 sccm 10% SiH₄ + He. The power levels are 10, 50, 75, and 110W. The spectra are normalized with respect to the maximum intensity of mass 31, and the three highest power spectra are offset from the baseline for viewing clarity. For each peak group there is a tendency for the lower mass peaks to increase at higher power levels as the higher mass peaks decrease. At 10W, there are peaks that exist at masses 63-65 that disappear at higher power levels. For the first peak group (28-33 m/z), the peak intensity of mass 28 increases with increasing power, until it becomes larger than mass 31 at 110W.
Figure 4.3a- Mass 31 normalized mass spectra of multiple Si atom molecular ions, 20-120 m/z. 10 sccm 10% SiH4 + He flow rate injected downstream, 13.56 MHz, 75W, 200 sccm He in the plasma tube, 300 mTorr, mass spectrometer port #1, ionizer turned off.
Figure 4.3b- Mass 31 normalized mass spectra of multiple Si atom molecular ions, 120-240 m/z. 10 sccm 10% SiH₄ + He flow rate injected downstream, 13.56 MHz, 75W, 200 sccm He in the plasma tube, 300 mTorr, mass spectrometer port #1, ionizer turned off.
Figure 4.3c- Mass 31 normalized mass spectra of multiple Si atom molecular ions, 240-340 m/z. 10 sccm 10% SiH₄ + He flow rate injected downstream, 13.56 MHz, 75W, 200 sccm He in the plasma tube, 300 mTorr, mass spectrometer port #1, ionizer turned off.
Figure 4.4a- Mass 31 normalized mass spectra of multiple Si atom molecular ions measured at different power levels, 25-95 m/z. 200 sccm He in the plasma tube, 10 sccm 10% SiH4 + He, 300 mTorr, mass spectrometer port #1, ionizer turned off.
Figure 4.4b- Mass 31 normalized mass spectra of multiple Si atom molecular ions measured at different power levels, 105-165 m/z. 200 sccm He in the plasma tube, 10 sccm 10% SiH₄ + He, 300 mTorr, mass spectrometer port #1, ionizer turned off.
4.3.3 Deposition Rate

Figure 4.5 shows plots of the mass 30 signal intensity as a function of power normalized with respect to the 0W signal level. It shows that the normalized silane signal intensity is constant for positions 2 and 3, while position 1 shows a 40% decrease once the plasma is ignited. Figure 4.6 compares the effect of deposition rate and change in mass 30 signal loss as a function of plasma power. The deposition rate shows an approximately linear dependence on power. The signal loss percentage is defined as the amount of signal decrease for a mass signal between plasma off and plasma on conditions. The percentage loss data is divided by 10. The consumption of mass 30 shows saturation at about 70% around 50W.

Figure 4.7 is a plot of the deposition rate for a-Si:H films as a function of electron density derived from double Langmuir probe measurements under similar operating conditions, except that there is no SiH₄ flow. The pressure is 300 mTorr, with 200 sccm He feedstock gas in the plasma tube, and 10 sccm 10% SiH₄ + He injected downstream. The relation follows a logarithmic behavior with a correlation coefficient of 0.954, for a characteristic deposition rate of 3.79 Å/m and a characteristic electron density of 1.42 x 10⁷ cm⁻³.

Figure 4.8 demonstrates the relation between the deposition rate of a-Si:H as a function of plasma tube to sample growth distance. The growth conditions are 50W at 13.56 MHz, 200 sccm He plasma feedstock gas, 10 sccm 10% SiH₄ in He, 300 mTorr, and 200°C substrate temperature. The deposition rate decreases logarithmically as a function of substrate distance, with a regression fit factor of 0.993. The logarithmic relation holds even for samples grown upstream from the SiH₄ injection point. A logarithmic regression fit of the curve gives the relation,

\[ d(x) = d_0 \exp\left(\frac{x}{\Lambda}\right) \]

(4.1)
Figure 4.5 - Normalized 30 m/z mass spectrometry signal as a function of power at all three sampling positions. 13.56 MHz discharge, 50W, 200 sccm He in the plasma tube, 10 sccm 10% SiH4 + He, 300 mTorr. The three sampling positions are, #1 2.54 cm, #2 13.35 cm, #3 39.37 cm.
Figure 4.6- Deposition rate and decrease in mass 30 loss as a function of power. 50W, 13.56 MHz discharge, 300 mTorr, 200 sccm He in the plasma tube, and 10 sccm 10% SiH4 + He in the plasma tube.
Figure 4.7 - a-Si-H deposition rate as a function of ne. 13.56 MHz discharge, 300 mTorr, 200 sccm He in the plasma tube, 10 sccm 10% SiH4 + He injected downstream.
Figure 4.8 Deposition rate as a function of plasma tube opening, growth signal position, distance. 200 sccm He in the plasma tube, 10 sccm 10% SiH₄ + He, 50W, 13.56 MHz, 300 mtorr.
where, \( d \) is the deposition rate, \( x \) is the distance from the end of the plasma tube, \( d_0 \) is the deposition rate at the plasma tube, 233.3Å/m, and \( \lambda \) is the characteristic length, 4.476 cm.

Figure 4.9a shows the relation between deposition rate and silane gas flow, at 50W power, and at a 13.4 cm distance between the plasma tube and the sample holder. The curve shows a deposition rate maxima around 10 sccm 10% SiH₄ + He, with a rapid drop towards lower flow rates and a gradual decrease towards higher flow rates. The curve is an inverse parabolic fit, which is described in more detail below. The bonded hydrogen content also increases with the increasing silane flow rate, see Fig. 4.9b.

### 4.3.4 Film Properties

Figure 4.10 shows the IR absorption features of an a-Si:H film. All of the features of the plot are associated with Si-H modes. The film was grown at 250°C, with 200 sccm He plasma feedstock gas, 50W power, 300 mTorr, 10 sccm 10% SiH₄ + He, grown 2.54 cm from the plasma tube. The dominant feature is the Si-H bending mode, SiH(b) at 630 cm⁻¹. There is the SiH stretching mode, SiH(s), at 2000 cm⁻¹. For heavily hydrogenated films there is a SiH₂ stretching mode, Si-H₂(s), at 2100 cm⁻¹, and two chain-like SiH₂ scissors wagging modes, at SiH₂(w), at 850 and 900 cm⁻¹.

Figure 4.11 shows the SiH content in a-Si:H films as a function of plasma power, for samples grown 13.3 cm downstream from the plasma tube with the standard pressure and flow rates described in section 4.2. This plot displays an abrupt increase in the bonded hydrogen content between 20 and 27W, with a maximum hydrogen content of about 1.9 x 10²² cm⁻³, or 27%. Above 27W it appears that the hydrogen content is constant, but below 20W there is a positive relation between power and hydrogen content.

Figure 4.12 shows the effect of He flow rate on the hydrogen content of a-Si:H films grown under the standard power and pressure conditions described in section 4.2. In general, the hydrogen content decreases with increasing He flow rate. Figure 4.13 is a plot of the silicon dihydride group concentration in various films as a function of the film
Figure 4.9- a) a-Si-H deposition rate as a function of 10% SiH₄ + He flow rate. 13.56 MHz discharge, 50W, 300 mTorr, 200 sccm He in the plasma tube, 13.3 cm downstream sample growth position. b) Si-H concentration in a-Si-H as a function of 10% SiH₄ + He flow rate. 13.56 MHz discharge, 50W, 300 mTorr, 200 sccm He in the plasma tube, 13.3 cm downstream sample growth position.
Figure 4.10: Infrared spectrum of a highly hydrogenated amorphous Si film.
Figure 4.11- Plot of Si-H concentration in a-Si-H films as a function of plasma power. 13.56 MHz discharge, substrate positioned 13.3 cm downstream, 200 sccm He in the plasma tube, 300 mTorr, 10 sccm 10% SiH₄ + He injected downstream.
Figure 4.12- Effect of He flow rate on the SiH concentration in a-Si-H films.
Figure 4.13- Plots of the silicon dihydride group concentration in various films as a function of the films deposition rate.
deposition rate. The films were grown at different powers and growth positions, but at the standard flow rates and pressure listed in section 4.2. The dihydride concentration has a linear behavior and a correlation coefficient of 0.994.

4.4 Discussion

There are several channels in which SiH₄ molecules may be diverted in the remote PECVD reactor. The essential first step in understanding the process is to enumerate these channels. Figure 4.14 shows channels by which silane is converted into a-Si:H and other products. The overall mass balance of the equation is given in equation (4.2), where (1) is the injected SiH₄ flow rate, (2) is the film growth rate, (3) is the unconsumed SiH₄ flow rate, and (4) is the flow rate of SiₓHₙ clusters:

\[(1) = (2) + (3) + (4)\]  \hspace{1cm} (4.2)

or

\[\text{SiH}_4(\text{in}) = \text{Film} + \text{SiH}_4(\text{out}) + \text{Si}_x\text{H}_y(\text{out})\]  \hspace{1cm} (4.3)

![Schematic diagram of Si mass balance between injected silane and Si film growth.](image)

Figure 4.14- Schematic diagram of Si mass balance between injected silane and Si film growth.

Equation 4.3 is different from previous discussions of the remote PECVD process in that it includes a term for the polysilane reaction product. The significance of this term is discussed below. This discussion first examines the silane excitation mechanisms in the
remote PECVD reactor. Then it investigates the significance of gas phase products formed from SiH₄ excitation. Next it discusses the a-Si:H deposition reaction orders with respect to electron concentration and SiH₄ flow rate. Then it explores the possible effect of deposition precursors on hydrogen content of a-Si:H films grown by remote PECVD. Finally, the discussion examines issues with the measurement of silane radicals using the mass spectrometer.

4.4.1 Silane Excitation Mechanism

Figure 4.1 shows the effect of additions of silane on a He plasma afterglow. The most notable change is that the intensities of all He lines decrease because energy is being diverted into the excitation of SiH₄. It is clear from the data presented that the plasma undergoes chemical changes upon the addition of silane. The change in intensity ratio of the two He lines indicates a change in population of species that excite He. For the 5876Å intensity decrease relative to the 5015Å line, the explanation can be either 1) the excitation rate of He to its 3⁢D drops relative to 3¹P, or 2) the 3⁢D state is preferentially relaxed by another process such as SiH₄ Penning excitation. In order to evaluate the likelihood of the first mechanism, information is required about the lifetime of excited He states. The second explanation requires that He⁺/SiH₄ Penning ionization cross-sections of be on the order of the He⁺ Penning self-ionization cross-section. The 3⁢D excitation rate change explanation is not likely, since the excitation occurs in the plasma tube where the SiH₄ concentration is negligible.

Figure 4.2 demonstrates that the population of excited states of H and SiH are affected the same mechanism. The plot shows a maxima around 2 sccm 10% SiH₄ + He, then drops to background levels near 10 sccm. The increase in intensity from 0 to 2 sccm 10% SiH₄ + He shows that the excitation process is rate limited by the SiH₄ content. The decrease at higher flow rates means that the process is limited by the exciting species, because the exciting species are relaxing through another process. The exciting species
could be electrons in the downstream glow or He*-tron. Since the intensity vs. silane flow rate
data does not follow the behavior of deposition rate or consumption of silane, these lines
are not good indicators for process control, since SiH is known not to be a precursor in
glow discharge systems.

The ion mass spectrometer data presented in Fig. 4.3 demonstrates that the
ionization source in the afterglow discharge is not necessarily electrons, because the plasma
excitation pattern of silane species is much different from that of the neutral silane cracking
pattern detected in the mass spectrometer using the electron beam. The most important
feature is that mass 31 is about 100% larger than mass 30. Mass 30 of the cracking pattern
of neutral silane is normally 20% larger than mass 31, (Fig. 4.15). There are some
physical differences in the ion generation of the mass spectrometer ionizer and the plasma.
First, the electron energy is 70 eV in the mass spectrometer, but only about 3 eV in the
reactor. Furthermore, species in the mass spectrometer typically undergo at most one
ionization event, while in the reactor, multiple ionization events can occur.

A plot of electron impact ionization cross-sections for SiH₄ shows that the cross-
section for SiH₂⁺ is always greater than that for SiH₃⁺ [4.4]. This means that the SiH₂⁺
signal must be greater than SiH₃⁺ signal if electrons are the primary SiH₄ ionization
source. Disilane and other polysilanes (polysilanes are defined as all Si-H compounds with
at least 2 Si atoms) have been shown to produce a 2:1 ratio of SiH₃⁺ to SiH₂⁺ when
fragmented by electrons [4.5,4.6]. If 90% of the mass 28-31 signals were coming from
polysilanes (the required concentration to obtain the 2:1 ratio), the disilane signal intensities
would have to be at least five times higher than the mass 28-31 signal [4.7]. Finally, it
might be argued that SiH₂⁺ could be selectively removed from the sampling gas as it travels
the length of the sniffer tube due to wall collisions, since it has a greater sticking coefficient
than SiH₃⁺. However whenever an ion collides with the wall it is electrically neutralized.
Thus sniffer tube wall collisions reduce all ion populations proportionally to their initial
Figure 4.15-Cracking Pattern of Silane. 70eV electron beam.
concentration. It is therefore necessary to consider other mechanisms that contribute to silane ion excitation.

The sources of energy in the reactor are 1) energetic electrons, 2) thermal energy, 3) photons, 4) electronically excited molecules, and 5) ions. Electrons have been eliminated in the discussion above. Thermal energy can be excluded, since the reactor temperature is too low for pyrolytic reduction of silane, and the population of 10 eV photons is low enough to be neglected. The only remaining sources are ions and metastables. He$^+$ could provide ionization through charge exchange, and He$^*$ are known to excite ground state molecules through Penning ionization.

It is possible to estimate the reaction cross-section for two body collisions between electrons, He$^*$, and SiH$_4$ [4.8]. The estimated cross-sections are listed below for Penning and electron impact ionization of SiH$_4$:

$$\text{He}^* + \text{SiH}_4 \rightarrow \text{He} + \text{SiH}_x^+ + e^-, \ (0 \leq x \leq 3) \quad \sigma = 6 \times 10^{-15} \text{ cm}^2 \quad (4.4)$$

$$\text{e}^- + \text{SiH}_4 \rightarrow \text{SiH}_x^+ + 2e^-, \ (0 \leq x \leq 3) \quad \sigma = 3.5 \times 10^{-16} \text{ cm}^2 \quad (4.5)$$

$$\text{e}^- + \text{He} \rightarrow \text{He}^* + \text{e}^- \quad \sigma = 4 \times 10^{-18} \text{ cm}^2 \quad (4.6)$$

where, the data for (4.5) is from Srivastava [4.4], and the data for (4.6) is from McDaniel [4.9]. Equation (4.6) is included primarily for reference with the cross-sections of SiH$_4$ excitation. The ionization cross-section via He metastables is about 20 times greater than electron impact ionization of SiH$_4$. Data concerning the silane ion products of Penning ionizations has not been published. However, Penning reactions between He$^*$ and SiH$_4$ can explain the reactor-generated ion mass spectra. He$^+$ and SiH$_4$ reactions could also be the source of the different ion spectra, but not enough is known about their reaction cross-sections.

There is some information about the relative cross-sections for the production of He$^+$ ions and 2$^1$P metastable He formed by electron impact. The cross-section for the formation of metastables is about 250 times larger than the ionization cross-section [4.10].
This implies that the population of $\text{He}^*$ is greater than $\text{He}^+$, therefore it might be said that metastable excitation dominates over ion excitation. However, there are two caveats that must be observed. First, these species are generated externally to the chamber then transported to the reaction region by diffusion, so the lifetimes of these species might be important if the $\text{He}^+$ and $\text{He}^*$ lifetimes differ by more than two orders of magnitude, and the $\text{He}^*$ lifetime is less than 3 msec. In addition, if the $\text{He}^+$ charge exchange reaction cross-sections with $\text{SiH}_4$ are orders of magnitude larger than the $\text{He}^*$ $\text{SiH}_4$ cross-section, then the higher metastable population is not critical.

Previous experiments have shown that a-$\text{Si:H}$ films can be deposited by extracting active species from rf-excited He discharges in remote PECVD reactors [4.11,4.12]. The microwave discharge has a glow region that is maintained only within the waveguide and its wings. It has been observed that a-$\text{Si:H}$ films can be deposited from He discharges using rf excitation, but that these films cannot be deposited using microwave discharges. On the basis of Fig. 4.3, these results are consistent with the conclusions of the previous studies. The density of charge particles, i.e., electrons, transported out the plasma excitation region of the rf plasma due to the electrode geometry is sufficiently high to promote a heterogeneous CVD interaction. The density of electrons extracted from the microwave plasma is insufficient to promote measurable film deposition.

Because charged species are required to grow a-$\text{Si:H}$ films, Penning reactions do not contribute to film growth. These results demonstrate that if Penning ionization is indeed the source of ion production, then it is not directly related to film growth. However, if the ion spectrum is a function of $\text{He}^+$ charge exchange, then it may be possible for the ion spectra to provide indications of reaction precursors.

### 4.4.2 Products of Silane Decomposition

The mass spectrometer data shows that the $\text{SiH}_4$ injected is being converted into another form when the plasma is ignited, see Fig. 4.6 and Fig. 4.5. Figure 4.5 shows that
the decrease is substantially larger for position 1 compared with the other sampling positions. The larger decrease of position 1 corresponds almost exactly to the 40% predicted decrease in SiH4 concentration due to backdiffusion. Section 9.2 examines backdiffusion in more detail. It shows that the interaction of SiH4 and the plasma is SiH4-limited, but that does not necessarily mean that the a-Si:H deposition reaction is SiH4 limited.

In Fig. 4.6 it is important to note that the deposition rate is linear while the mass 30 signal is not. The two curves show that deposition rate and mass 30 intensity are not proportional, and therefore the mass 30 intensity is not a direct indication of deposition rate. It demonstrates that there is another channel for silane consumption. At 50W the signal intensity of the daughter species has decreased by about 75% throughout the chamber and the measured deposition rate is 103 Å/min at 2.5 cm downstream. For the aforementioned deposition rate the flux density of incorporated mono-atomic Si-bearing molecules is 5.2 x 10^{16} \text{ cm}^{-2} \text{ s}^{-1}, assuming a Si atomic density of 5.00 x 10^{22} \text{ cm}^{-3}. For a 300°C gas temperature, the deposition rate is equivalent to about 110% of the SiH4 concentration in the chamber (4.6 x 10^{16} \text{ cm}^{-3}). The reason is that the flux density for deposition is larger than the flux density of injected silane is because the 103 Å/min deposition rate is not the mean deposition rate for the reactor. Since this does not properly account for total SiH4 consumption, it is necessary to estimate the total consumption of SiH4 through film deposition, Fig. 4.8.

In order to determine the total fraction of SiH4 lost to deposition throughout the reactor, it is necessary to develop a procedure to determine the steady state loss rate. The mass spectrometer data indicates the amount of SiH4 depleted by subtracting the mass spectrometer signals of plasma on from plasma off conditions. The deposition rate plot of Fig. 4.8 demonstrates the rate at which SiH4 is consumed in different parts of the reactor,
and can be used to determine the total amount of Si incorporated into a growing film through the following derivation.

The flux density of consumed Si$_1$H$_x$ species in the chamber can be simply stated as the average incorporated flux density in the chamber, $<\text{jinc}> \equiv <d>\rho$, where $<d>$ is the spatially averaged steady state deposition rate, and $\rho$ is the atomic density of Si. The key to solving for $<\text{jinc}>$ is to find $<d>$. The deposition rate of the radial dimension accounts for deposition on the chamber end flanges. Accounting for these terms leads to,

$$<d> = \frac{\int_{0}^{z_1} d(z)2\pi r_c \, dz + d_0\pi r_c^2 + d(z_1)\pi r_c^2}{2\pi z_1 r_c + 2\pi r_c^2}$$  \hspace{1cm} (4.7)$$

where, $z_1$ is the chamber length, $r_c$ is the chamber radius. Because the deposition rate at $z_1$ is small, (0.007% of the plasma tube end deposition rate), the third term of the numerator is neglected. Solving the integral of equation 4.7 for $d(z)$ defined in equation 4.1 yields,

$$2\pi r_c \int_{0}^{z_1} d_0 \exp\left(-\frac{z}{\lambda}\right) = 2\pi d_0 r_c \lambda \left(1 - \exp\left(-\frac{z}{\lambda}\right)\right).$$  \hspace{1cm} (4.8)$$

Substituting equation 4.8 into equation 4.7 and simplifying gives the result,

$$<d> = d_0 \left(\frac{2\lambda \left(1 - \exp\left(-\frac{z_1}{\lambda}\right)\right) + r_c}{2(z + r_c)}\right)$$  \hspace{1cm} (4.9)$$

For the experimental conditions 200 sccm He plasma tube feed, 10 sccm 10% SiH$_4$ + He, 50W 13.56 MHz power, and 300 mTorr, and chamber dimensions of 43 cm length, and 7.6 cm chamber radius, $d_0$ of 230 Å/m, $\lambda$ of 4.48 cm, and surface area about 2400 cm$^2$, yield $<d> = 38.4$ Å/m. This estimate does not account for non-uniformity due to shadowing, and the extra surface area of the sample holder, ports, and gas dispersal rings. Using the Si atomic density mentioned above, a mean flux density in the chamber of 1.8 x 10$^{16}$ cm$^{-2}$ s$^{-1}$ is required. Therefore conversion of injected SiH$_4$ into a-Si:H is about 40% to 55%.
The derivation above shows that as much as 55% of SiH₄ is consumed by the growing film. The question prevails of the disposition of the remaining 45% of the injected SiH₄. Pumping all of the remaining SiH₄ from the reactor does not explain the typically five fold decrease in the mass spectrometer signal between the no plasma condition and a 75W discharge. Since there is a difference between the fraction converted into a-Si:H and the fraction consumed, there must be another consumption channel that accounts for the remaining 25%. One example is silane conversion into another Si-containing species, for example polysilane SiₓHᵧ (x>1), described in subsection 4.3.2.

It is possible for polysilane species to contain a large fraction of Si atoms while having low levels compared to silane signal levels. First, there is the linear relation between each particle for species SiₙHₓ detected, the number of Si atoms n. A corollary to that is n is the number silane molecules consumed to manufacture each SiₙHₓ. Therefore, the mass spectrometer signal for a Si₄Hₓ species would be 4 times smaller than the original silane signal. The other factor is that the differences in branching ratios for successively larger Si groups decrease. Assuming that all branching ratios are the same, the excitation cross-sections for each species are the same, and that the molecules are Si alkane-like chains are saturated; the average branching ratio would be the inverse of the number of possible H bonds on the material + 1, or 2n + 3, where n is the number of Si groups in the chain. Therefore the signal defining the number of Si atoms in each unit of signal is:

\[
\# \text{ Si atoms} = \frac{\text{signal} \times \# \text{Si atoms in chain}}{\text{average branching ratio}} \tag{4.10}
\]

or

\[
\# \text{ Si atoms} = \text{signal} \times n (2n + 3).
\]

For example, for a peak group Si₆Hₓ, the average signal intensity for the peak group would be multiplied by a factor of 90 to account for all of the silane molecules consumed.

The following example illustrates the determination the of ratio of Si within polysilane species to the Si within the SiH₄ source. Figure 4.3 shows the mass spectrum
ion signal normalized with respect to mass 31. The spectrum shows the relative ion fluxes for all Si-containing species generated in the chamber from neutral precursors. Assuming that the ionization cross-sections are roughly the same (within a factor of 2), it becomes a matter of finding the number of peaks in each peak group. By including all of the peaks for peak groups larger than silane itself, using the method described previously, the total count is 7.2. The silane peaks yield a count of 2.8. This indicates that about 2.6 times more Si atoms reside in the multi-Si ion clusters than in the silane. By comparison, the loss of signal intensity of silane with respect to 75W shown in Fig. 4.5 would show that the silane signals drop around 80%, implying that 4 times as much silane is being consumed than remains unconverted.

The difference between 4 and 2.6 is not unreasonable considering differences in excitation cross-sections for the different fragments and the mass-dependent sensitivity of the quadrupole filter since there is no guarantee of uniform sensitivity. One source of error might be that electron impact ionization of a multi-Si species can fragment the compound into smaller species, only one of which is ionized. Then it could be argued that the error is caused by non-detection of these non-ionized groups. However, the afterglow permits multiple ionizations since the non-ionized species remains in the presence of the ionizing source. Even though there is some error in the estimate the argument clearly shows that a significant fraction of the silane consumed under conditions for growth of a-Si:H is converted into polysilane instead of deposition.

The polysilane production channel is obviously large enough that it needs to be considered in some detail. Even though neutral disilane species are not reactive, the polysilanes are subjected to the same excitation processes as silane. It is reasonable to argue that if polysilane can be so excited, they can be as reactive as monosilane radicals. Since they exist in a similar concentration as SiH₄, it is reasonable to conclude that they
contribute to a-Si:H film growth. Therefore it is necessary to redefine the mass balance equation (4.3) to account for the polysilane contribution to film growth.

\[
\text{Film Mass Balance: } \quad \text{Film} = \text{SiH}_4(\text{Film}) + \text{Si}_x\text{H}_y(\text{Film}) \quad (4.11)
\]

\[
\text{Cluster Mass Balance: } \quad \text{Si}_x\text{H}_y = \text{Si}_x\text{H}_y(\text{Film}) + \text{Si}_x\text{H}_y(\text{out}) \quad (4.12)
\]

\[
\text{Silane Mass Balance: } \quad \text{SiH}_4(\text{in}) = \text{Si}_x\text{H}_y + \text{SiH}_4(\text{Film}) + \text{SiH}_4(\text{out}) \quad . \quad (4.13)
\]

Equation (4.11) shows the contribution of the two silicon sources, equation (4.12) shows the balance of polysilane formation and consumption, while equation (4.13) shows the sources and sinks of SiH\textsubscript{4}. Combining these three equations yields the overall mass balance equation of (4.3). Even though the net result is the same, it shows polysilanes need to be included when performing the mass balance on a-Si:H deposition.

Earlier work did not detect polysilanes in the 5.1 cm diameter reactor [4.13]. It is possible that the narrower reactor does not allow for measurable polysilane formation. SiH\textsubscript{2} radicals are quite reactive, since they have the ability to break Si-H bonds and insert themselves [4.14]. Therefore they react as readily on a silicon surface as with another Si-containing species in the gas phase. If a SiH\textsubscript{2} radical collides with another Si molecule before encountering a surface it reacts with it, thus removing it from the deposition reaction. Since the volume/surface area ration decreases with diameter, a 5.1 cm diameter chamber will be more efficient at inserting SiH\textsubscript{2} into film surface than the 15 cm diameter reactor. This is one reason that it may be difficult to detect polysilanes in narrower diameter chambers. The other possibility is that experiments in the 5.1 cm reactor used SiH\textsubscript{4} diluted in Ar instead of He. Argon may compete with SiH\textsubscript{4} for reactions with excited He, thus limiting SiH\textsubscript{4} radical production. The lower production rate inhibits polysilane production.
4.4.3 Reaction Orders and Efficiency

It is known that for low temperature plasma-enhanced deposition of amorphous silicon the overall deposition reaction is,

\[ \text{SiH}_4 + e^- \rightarrow \text{a-Si}:\text{H} \quad (4.17) \]

with the overall parallel gas phase insertion reaction,

\[ \text{SiH}_4 + e^- + \text{Si}_y\text{H}_x \rightarrow \text{Si}_(y+1)\text{H}_z \quad (4.19) \]

where \( y \geq 1 \). These reactions account for all polysilane molecules, since they grow through sequential reactions, and the same excitation reactions are needed to fragment each silane molecule. The functional form of the reactions are shown in curve fitting plots of product concentration as a function of reactant concentration. These relations are displayed in the curves showing the a-Si:H deposition rate as a function of electron density Fig. 4.7, and SiH\textsubscript{4} flow rate, Fig. 4.9.

It is possible to derive the form of the rate equation based upon the following arguments. Since both reactants of the insertion reaction are from the same source, the reaction is higher than first order \([4.15]\). Since the film is a solid phase product in a gaseous reaction, the concentration term in the reaction rate equation is unity. The loss probability requires the addition of higher order terms in the relation such as listed in equation \((4.19)\). This is reasonable, since the growth of the Si clusters requires two Si-containing molecules. Each reaction that adds a Si atom to the cluster occurs in temporally distinguishable steps. The relations displayed in Figs. 4.9 and 4.7 show the order of the reaction by the equation that fits the curve. The silane partial pressure plot of Fig. 4.9 shows linear behavior at low silane concentrations, however at higher concentrations, the probability for gas phase SiH\textsubscript{4}/SiH\textsubscript{2} insertion reactions increases. Kinetic data at several reactant concentrations is required to determine what is the rate law, but since it is a mechanism that involves two types of parallel reactions it should follow a form like,
\[ \frac{dn_{\text{SiH}_4}}{dt} = -k_1[\text{SiH}_4]\text{[e-]} - k_2[\text{SiH}_4]^2\text{[e-]} - \sum_{i=3}^{\infty} k_i[\text{SiH}_4][\text{Si}_{(i-1)}\text{H}_x]\text{[e-]} . \] (4.20)

Formation reactions are neglected in equation (4.20). The equation shows a reaction term for growth of a-Si:H from silane precursors, and subsequent formation of Si clusters through insertion reactions of electron excited silane species. The rate constants are \( k_1 \) for the a-Si:H reaction, \( k_2 \) for the disilane formation, and \( k_i \) for the formation of the Si molecule containing \( i \) Si atoms. It does not matter if chains insert themselves into other chains, since the same amount of silane and the same number of reaction steps are required. Other reactions, such as hydrogen transfer in SiH\(_3\) and SiH\(_4\), do not affect the overall outcome of the reactions, since they result in the same products as reactants. Fragmentation of larger chains is not considered in this scheme, but it does not significantly contribute to the overall kinetics, since the source gas is SiH\(_4\).

By curve fitting using the appropriate functions on Figs. 4.7 and 4.9, it is possible to determine the relative efficiencies of electrons and silane, respectively, for growing a-Si:H films. By converting the deposition rate and steady state SiH\(_4\) partial pressure as determined from the mass spectrometer data, and using the electron density estimate from the Langmuir probe data, \( n_e \), it is possible to empirically determine the reaction orders with respect to each reactant. Equation (4.21) is the logarithmic regression fit for the deposition rate as a function of electron density. The prefactor for equation (4.21) is 3.79 Å/m translates into a gas phase Si precursor flux density of \( 1.91 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1} \),

\[ d = 3.79 \text{ Å/m} \ln\left( \frac{n_e}{1.42 \times 10^7 \text{ cm}^{-3}} \right) \] (4.21)

The Si precursor concentration term can be used instead of the deposition rate to find the number of source gas molecules consumed for a given electron density value. For example, for 10 sccm SiH\(_4\) flow rate, if the electron density in the vicinity of the sample is \( 10^9 \text{ cm}^{-3} \), the concentration of silane precursors being consumed is \( 2.86 \times 10^8 \text{ cm}^{-3} \), or a deposition
rate of 16 Å/m. The logarithmic dependence demonstrates that the process becomes less efficient as the electron density increases at producing deposition precursors. This is because the reaction becomes limited by the silane concentration. Therefore, larger electron concentrations mean a larger fraction of electrons relax through non-deposition channels.

The silane efficiency relation is higher than first order due to the parallel consumption of silane into larger polysilane. The equation has the form of,

\[
    d = \kappa \frac{n_{SiH4}}{1 + \kappa' n_{SiH4}^2}
\]  

(4.22)

where \(\kappa\) and \(\kappa'\) are fitting parameters for the equation, see Fig. 4.9. This equation accounts for the increasing likelihood of Si cluster reactions, at the expense of film deposition. The silane partial pressure may be determined by multiplying the percentage decrease in the mass 30 signal between discharge on and off levels by the silane partial pressure with discharge off. Fitting Fig. 4.9 to this equation yields \(\kappa = 2.5 \text{ Å min}^{-1} \text{sccm}^{-1}\), and \(\kappa' = 10^{-2} \text{sccm}^{-2}\).

4.4.4 Bonded Hydrogen Groups in a-Si:H

Tanaka and Matsuda proposed that the deposition mechanism governing film morphology is based on the surface mobility of reactive silane species, and that hydrogen termination of the network provides increased mobility for certain radicals [4.16,4.17]. In their experiment they measured the growth rate and morphology of films grown on well characterized surfaces with known degrees of hydrogen-terminated Si and controlled silane radical concentrations [4.16]. They found that under conditions in which the hydrogen was removed from the surface, the deposition rate using SiH3 increased dramatically, (an order of magnitude in some cases). They theorized that for SiH3 incorporation, a prior step of removing a hydrogen atom is required, while for SiH2 the radical can abstract hydrogen and insert itself without assistance. In addition, the radicals with higher mobility were shown to produce a denser Si network.
The abrupt increase noted in Fig. 4.11 shows a discontinuous increase in the [SiH] that may be argued along the lines of Tanaka and Matsuda's work. At lower power levels the dominant species arriving at the substrate may be SiH₃. Since SiH₃ requires a bare Si site to react, the growth of the network is more ordered and contains less bonded hydrogen, since H has to be removed for growth to continue. They noted that the SiH₃ radical has a longer lifetime compared with other silane radicals, thus it can diffuse further from its generation site before it is consumed. When the incoming flux is SiH₃ dominated, the film contains less hydrogen since they grow more slowly. SiH₂ on the other hand, is likely to react with the first Si-containing particle it encounters. Therefore it needs to be generated in the vicinity of the film to be incorporated. However, once the plasma intensity is great enough to generate SiH₂ in the vicinity of the growing film, the surface state of the film is no longer an issue to film growth. Network propagation no longer requires hydrogen removal, so the hydrogen incorporation probability increases. A more complete study is needed to confirm the discontinuous behavior.

4.4.5 Deposition Precursors

The mass spectrometer experiments carried out to date have yet to conclusively determine what are the α-Si:H deposition precursors for the remote PECVD. The experimental technique used to detect the presence of radicals and other metastable species is appearance potential mass spectrometry. The primary factor that inhibits measurement is the geometric configuration of the mass spectrometer sniffer tube. The design leads to preferential filtering of the deposition precursors. This subsection demonstrates the filtration of deposition precursors from the sampling beam in the mass spectrometer.

The sniffer tube for the mass spectrometer is a 1.6 cm diameter stainless steel tube and is 8.9 cm in length. The molecules pass through a 150 μm orifice in the top of the tube and travel the length of the tube on their way into the ionizer region of the mass spectrometer. After traversing the tube, they pass through a volume of the gate valve body,
The functions derived above can be applied to the sniffer tube used for the mass spectrometer. Assume that $\alpha$ is 0.05 for the species of interest. For the geometry mentioned above, $T_{snf}$ is 0.11 or about an order of magnitude decrease in concentration. $T_{gv}$ then is a ratio of the aperture radius over the traversing distance squared, or 0.001, a three order of magnitude decrease. Therefore the total transmission function is $T = c = c_0 \times 10^{-4}$, or a four order of magnitude decrease in the flux entering the sniffer tube. For SiH$_2$, $\alpha = 0.5$ has been estimated at, $T_{snf} = 0.001$ and $c = c_0 \times 10^{-6}$. Filtering of He* is even higher because wall collision relaxes He, so it can be assumed that $\alpha$ is unity, hence $c = c_0 \times 6 \times 10^{-8}$. For silane however, the sticking coefficient is negligible so the sniffer tube transmission is unity, therefore the transmission function is $c = c_0 \times 10^{-3}$. This shows that the sniffer tube provides one to three orders of magnitude filtration for deposition precursors over their neutral parent species.

An additional experimental difficulty is the energy spread of the electron source. The electrons are generated by a square shaped filament through thermionic emissions and are accelerated towards the instrument axis by a wire cage in the shape of a cylinder with wires parallel to the axis. The filament is not uniformly shaped so emission is not necessarily uniform from all directions, and the distance between filament and axis differ, creating different E field intensities. These geometric deviations and a 3.5-4.0 V drop across the filament provide for a wide energy spread, at least as large as the filament voltage drop. For normal mass spectrometric measurements this is not an issue, but the difference in energy between ground state ionization and metastable ionization is typically 3-4 volts. The broad electron energy spectrum spreads any metastable peak across the shoulder of the main peak.

4.5 Summary

The discussion in this chapter has raised several points concerning the a-Si:H deposition reaction. Penning ionization contribute significantly to the reactor-generated
silane and polysilane ion signals, but does not significantly contribute to production of deposition precursors. It was also shown that about 50% of the silane injected into the chamber is incorporated into films, but a significant fraction (~25%) is converted into polysilanes that transport silicon from the reactor. It is assumed that the polysilane growth occurs through SiH₂ insertion reactions with other Si species. The overall reaction order is indeterminate because of polysilane production, but it shows a logarithmic-like dependence with respect to e- concentration. A reaction rate equation was proposed for silane consumption based upon the reaction products detected. It is proposed that the discontinuous increase in [SiH] may be related to the production of film incorporated SiH₂ radicals in the vicinity of the growing film. Finally, what exactly the precursors are and under what conditions they form cannot be conclusively determined due to the geometry of the mass spectrometer sniffer tube and its distance from the sampling orifice.

References


[4.7] This estimate takes into account a high mass sensitivity discrimination of the mass spectrometer based on past experience that have been able to change the intensities of mass 60-70 by a factor of two with respect to mass 28-31.


[4.14] The SiH₂/SiH₄ insertion reaction has a reaction probability of 0.99.


5 Microcrystalline Silicon Growth

The primary issue addressed in this chapter is how H₂ affects the chemical equilibrium of the He/SiH₄ afterglow in remote PECVD reactors. Additions of H₂ to the reactor alter the relative concentrations of silane radicals and ensure hydrogen termination of silicon surfaces. The degree of hydrogen termination determines the surface reactions that lead to network propagation. Tanaka and Matsuda showed that as the silicon surface loses surface bound hydrogen, the films change from a microcrystalline structure to an amorphous morphology [5.1]

5.1 Objectives

A study of the SiH₄/H₂/He plasma afterglow system was performed in order to show how the addition of H₂ modifies the gas phase chemistry to produce microcrystalline silicon (µc-Si) films. In the previous chapter it was shown that gas phase polymerization occurs under conditions that produce a-Si:H. Furthermore, it was discussed in the previous chapter that the larger chamber/plasma tube diameter ratio permits a greater degree of mixing of silane and the plasma afterglow. It is known that H₂ promotes crystalline phase formation from PECVD processes and that it plays a key role in surface processes on the substrate and on the growing film. The work presented here concentrates on how the Si/H ratio affects the gas phase chemistry. The addition of H₂ suppresses production of certain species. The possible effects this may have upon film growth are discussed.

5.2 Approach

A series of films were grown with 10 sccm 10% SiH₄ + He injected downstream, 300 mTorr pressure, a constant power level of 50W, substrate position 13.3 cm downstream, temperature of 250°C, and a plasma feedstock gas flow rate of 200 sccm with a composition including 0-40 sccm H₂ and the balance of He. In addition, for 0%, 10%,
and 30% H₂ plasma feedstock composition, mass spectrometry signals were measured between 25 and 65 m/z to detect the presence of polysilane species.

5.3 Results

Figure 5.1 shows the Raman spectrum between 400 and 550 cm⁻¹ of a silicon thin film deposited on fused silica substrates heated to 250°C, with 300 mTorr, 200 sccm He plasma tube feedstock gas, 5 sccm H₂, and 10 sccm 10% SiH₄ + He injected downstream. The film shows an Si-Si band centered at 480 cm⁻¹ which signifies a disordered material. There are no other peaks present. Figure 5.2 is a Raman spectrum for a silicon film deposited on a fused silica substrate with the same conditions as for Fig. 5.1, except for 30 sccm at H₂ injected downstream. The most prominent feature of this spectrum is a relatively narrow band centered about 520 cm⁻¹. This feature is associated with ordered Si-Si bonds. The 480 cm⁻¹ band also appears in this sample, but as a shoulder on the low wavenumber side of the 520 cm⁻¹ band. This plot has the same features with the same proportional heights at flow rates from 25 to 40 sccm H₂.

Figure 5.3 is a series of mass spectrum plots from 25 to 95 m/z in which the plasma gas H₂ composition is 0%, 10%, and 30% for 200 sccm total gas flow, 50W 13.56 MHz power. The spectrometer is set up to detect only the fragments of neutral species. The peaks around 30 m/z are attributed to silane fragmentation and those centered around 60 m/z are attributed to disilane fragmentation. Similarly the peaks located around 90 m/z are associated with trisilane. Most noticeably, the disilane and trisilane peaks decrease with increasing H₂ content in the plasma gas. On the 10% H₂ plot, there is an increase in m/z 63, but the ratios of peak intensities of 0 and 30% H₂ are similar. The ratio of 30/31 goes from 0.2 at 0% H₂ to 1.3 at 30% H₂, which is the ratio of m/z 30 to 31 for the silane cracking pattern. Figure 5.4 is a plot of the disilane peak intensities as a function of the fraction of H₂ in of the plasma feedstock gas. It shows that the m/z 58-60 intensities
Figure 5.1- Raman spectrum from 400 to 550 cm\(^{-1}\) of a silicon thin film deposited on fused silica substrates heated to 250°C, with 300 mTorr, 200 sccm He plasma tube feedstock gas, 5 sccm H\(_2\), and 10 sccm 10% SiH\(_4\) + He injected downstream.
Figure 5.3- Mass spectrum plots from 25 to 95 m/z in which the plasma gas H2 composition varies from 0, 18, and 58 sccm H2 out of 200 sccm total gas flow, 50W, 13.56 MHz, 250°C, 300 mTorr, 50 sccm H2, and 10 sccm 10% SiH4 + He injected downstream.
decrease by a factor of 3. The change in disilane peak mass intensities between 0 and 25 sccm H₂ show that mass 60 decreases by at least 0.5, while masses 58 and 59 decrease by at least a factor of 0.6.

5.4 Discussion

The most notable feature in Figs. 5.3 and 5.4 is the decrease in the disilane signal with increasing H₂ concentration. There are two explanations for the relationship between disilane signal level and μc-Si film growth. First, it is possible that disilane contributes to a-Si:H growth, and that lowering its concentration permits μc-Si growth. While neutral disilane is not reactive, radical forms of disilane and polysilanes are reactive. Polysilane surface mobility is not as high as the monosilane surface mobility, so polysilane incorporation is more likely to lead to a-Si:H network propagation. Reducing the polysilane concentrations reduces the a-Si:H growth reactions. The second explanation is that the disilane concentration is merely an indication of the SiH₂ concentration. SiH₂ incorporates itself into existing silicon networks through insertion reactions forming either multiple silicon atom molecules or silicon films. Such SiH₂ insertion leads to a-Si:H formation. If the disilane signal decreases it indicates that the SiH₂ concentration has also fallen.

There are two mechanisms by which hydrogen suppresses a-Si:H precursors. Such suppression can be expected as the system strives to achieve chemical equilibrium between SiH₄, SiHₓ (0 ≤ x ≤ 3), and hydrogen. In the first mechanism as the H₂ concentration increases, the gas phase chemical equilibrium of the SiH₄/H₂ system shifts towards silane species with higher degrees of hydrogenation [5.2,5.3]. The equations listed below are a subset of rate constants calculated by Kushner for an a-Si:H deposition model [5.3]. They indicate the relative reaction rates between hydrogen abstraction (5.1)-(5.3), and silane passivation (5.4)-(5.7) mechanisms. Atomic H forms H₂ by hydrogen abstraction from silane, leaving silane with lower degrees of hydrogenation, hence
of monochlorosilanes from the walls by He sputtering. The increase in the mass 63 intensity upon addition of H₂ shows that H₂ is stripping SiCl from the reactor walls. The drop in mass 63 at higher H₂ flow rates is merely caused by depletion of chlorosilanes from the walls, since the 58 sccm H₂ scan was made after the 18 sccm H₂ mass scan. Subsequent runs showed that mass 63 disappeared. Therefore, this indicates that addition of H₂ enhances etching of the silicon surfaces.

The plot in Fig. 5.2 shows that microcrystalline films may be deposited in this vacuum system under identical deposition conditions for other remote PECVD reactors [5.7-5.9]. The significance is that the growth data of other systems may be applied when discussing in-situ data collected in this system.

5.5 Summary

This chapter showed that microcrystalline films can be grown by the addition of hydrogen to the plasma feedstock gas. In gas phase reactions, hydrogen prevents disilane formation which is either a precursor or parallel reaction product of a-Si:H formation. The suppression mechanism occurs through either hydrogenation of silane radicals or dissipation of plasma power through alternative means to silane excitation. Hydrogen is an effective suppressant since its interactions with silane leave only other silane species; i.e., it is able to adjust the reaction driving forces without creating compositionally different species. Veprek has proposed a methodology for presenting the conditions that produce μc-Si films instead of a-Si:H films by defining the partial chemical equilibrium boundary between the two materials [5.10]. He proposes that SiH₂ production will promote a-Si:H growth over μc-Si.

References

6 Selective Silicon Epitaxial Growth

Methods for selective epitaxial growth of silicon utilizing plasma processing have not yet been closely examined. The work presented in this chapter examines how the precursor species decompose upon plasma exposure under conditions of selective epitaxial growth. Once it is known what is required to grow selective epitaxial films, it will be possible to design experiments to understand the mechanisms of selective growth and improve the process.

6.1 Objectives

This study concentrates on two objectives, determining the processing parameters for low temperature selective epitaxial film growth, and demonstrating SiH$_2$Cl$_2$ decomposition in the presence of a H$_2$/He discharge. By looking at the effect of the H$_2$ flow rate on the species SiH$_2$Cl$_2$ in the afterglow, it is shown how the SiH$_2$Cl$_2$ decomposes. Dichlorosilane decomposition must be known in order to understand which species are key for the selectivity mechanism. In addition, the study identifies possible gaseous species that may encourage the selective deposition mechanism, namely an ionic species that exists upon SiH$_2$Cl$_2$ decomposition with hydrogen.

6.2 Approach

A series of films were grown on patterned partially oxidized wafers to examine the selectivity of the deposition process. Each wafer is (100) Si and has a 1200Å thick patterned SiO$_2$ film grown by remote PECVD. The plasma power was 75W at 13.56 MHz with 100 sccm He injected through the plasma tube. A flow of 10 sccm of 1% SiH$_2$Cl$_2$ in He and a H$_2$ flow (0 to 50 sccm) was injected into the first set of downstream injection rings. The sample was mounted on a Si-coated copper block heater set to 300°C, and was positioned 3.8 cm downstream from the gas dispersal rings. The plasma grid assembly was installed over the end of the plasma tube with the end of the plasma grid about 3.2 cm
upstream from the gas dispersal ring. The grid was kept under electrically floating conditions.

The samples were examined with HRSEM to determine selectivity and morphology, and RHEED to determine the crystallinity of the films. TEM was performed on selected films to examine the defect density of epitaxial films. Mass spectrometry was used to determine the presence of gas phase species, to monitor the reactor atmosphere during deposition, and to determine the effect of H$_2$ addition on gas species production from 0-10 sccm H$_2$. In order to understand how H$_2$ reacts with SiH$_2$Cl$_2$, D$_2$ was substituted for H$_2$ to act as a hydrogen source tag, while the reaction products were monitored by mass spectrometry.

6.3 Results

Figure 6.1 shows SEM micrographs of the boundaries between the oxide and the grown c-Si layer. For samples deposited at flow rates lower than 50 sccm H$_2$, there is no selectivity; at the 50 sccm H$_2$ flow rate, the sample shows selective deposition, though some silicon nuclei exist on the oxide surface. Figure 6.2 shows RHEED patterns for the samples with 0, 20, and 50 sccm H$_2$ injected. The rings of the 0 sccm H$_2$ sample indicate a microcrystalline morphology, while the 20 and 50 sccm films exhibit a spot pattern associated with preferred orientation crystalline film growth. However, in order to achieve selective film growth with the above mentioned flow conditions, the films must be grown utilizing a predeposition wall loading step. Due to the low effective flow rate of SiH$_2$Cl$_2$ in the system, it is necessary to cover the reactor walls with reaction precursors in order to achieve reproducible selective film growth (10 hrs. of 5 sccm H$_2$, 10 sccm 1% SiH$_2$Cl$_2$ + He, 100 sccm He, and 75W). This will be discussed in detail at the end of the discussion, Section 6.4.
Figure 6.1- SEM micrographs of crystalline Si films deposited on patterned SiO$_2$/Si wafers. 75W, 13.56 MHz, 300°C, 300 mTorr, 10 sccm 1% SiH$_2$Cl$_2$ + He injected downstream, sample position 13.4 cm downstream. a) Film deposited with 0 H$_2$/200 He sccm plasma feedstock gas, b) Film deposited with 20 H$_2$/180 He sccm plasma feedstock gas, c) Film deposited with 50 H$_2$/150 He sccm plasma feedstock gas.
Figure 6.1

- Silicon Layer 0 sccm H₂
- Silicon Layer 20 sccm H₂
- Silicon Layer 50 sccm H₂
Figure 6.2- RHEED patterns of crystalline Si films deposited on patterned SiO2 / Si wafers. Same conditions as stated in Fig. 7.1. a) Film deposited with 0 H2 / 200 He sccm plasma feedstock gas, b) Film deposited with 20 H2 / 180 He sccm plasma feedstock gas, c) Film deposited with 50 H2 / 150 He sccm plasma feedstock gas.
Figure 6.3 is a TEM micrograph of a sample grown under conditions identical to those used to grow the film shown in Fig. 6.1c. The lower portion of Fig. 6.3 is the Si substrate, while the adjacent layer is the epitaxially grown film. The average layer thickness is about 350Å. Many stacking faults can be seen throughout the layer, some of which terminate at the surface and act as seeds for twinned crystallites. (The large disordered region in the upper portion of the image is the mounting adhesive.)

Figures 6.4 through 6.6 show the results of the mass spectrometric analysis. Figure 6.4 is the cracking pattern of SiH₂Cl₂ in He, covering 0-110 m/z, 70 eV electron beam energy and a high sensitivity factor (gain of 10⁹). The cracking of SiH₂Cl₂ produces di- and mono-chlorosilane peak groups (98-103, and 63-67 m/z, respectively), a HCl/Cl peak group, 35-38 m/z, and a silane peak group, 28-30 m/z. Figure 6.5 shows the change in intensities of these species from mass (25 to 110) as the H₂ flow rate increases. As the H₂ flow increases, there is a corresponding increase in the mono- and di-chlorosilane, silane, and hydrogen chloride peaks. However, new peaks at 31 m/z, and 39 m/z appear, and peak 37 m/z increases much more than other HCl peaks. Reactor generated ions are the major contribution to masses 31 (50%) and 37 (99%), and the only contribution to mass 39. The monochlorosilane peak intensities are about twice as large as the dichlorosilane peaks in the presence of the discharge, but are only half as intense for the SiH₂Cl₂ cracking pattern.

Figure 6.6 shows results of the same experiment in which deuterium, D₂, is substituted for H₂ in order to tag the hydrogen source in the detected species. The mass intensities of entirely deuterated species show the same relative intensities as the analogous protonated species for the H₂ case. The ratio of analogous deuterated and non-deuterated species is smaller than the ratio of injected D₂ to the 2H of SiH₂Cl₂. For example, mass 64 can only be derived from SiClH, and mass 65 can be derived primarily from SiCID and
Figure 6.3- TEM image of an epitaxial Si film deposited on a patterned SiO$_2$ / Si wafers, 800,000x, and 200kV. 75W, 13.56 MHz, 300°C, 300 mTorr, 50 H$_2$ / 150 He sccm plasma feedstock gas, 10 sccm 1% SiH$_2$Cl$_2$ + He injected downstream, sample position 13.4 cm downstream. Note the stacking fault and twinned grain on the surface of the growing layer.
Figure 6.4- Mass spectrum of SiH$_2$Cl$_2$ cracking pattern by electron impact ionization, 10-110 m/z. 300 mTorr, 200 sccm He, 10 sccm 1% SiH$_2$Cl$_2$ + He, 70 eV electron beam energy.
Figure 6.5- Mass spectrum of the effect of plasma tube H2 addition to SiH2Cl2 dissociation, 10-110 m/z. 75W 300 mTorr, 200 sccm He, 10 sccm 1% SiH2Cl2 + He, 70 eV electron beam energy.
SiClH$_2$. At 10 sccm D$_2$, the D$_2$/SiH$_2$Cl$_2$ ratio is 100:1, but the ratio of mass 65/ mass 64 is about 2:1.

6.4 Discussion

From the data presented in Figs. 6.5 and 6.6, it is clear that the addition of increasing amounts of hydrogen into the chamber along with the interaction of hydrogen with the plasma, strips Cl from the SiH$_2$Cl$_2$. The fact that the ion peaks of masses 37 and 39 appear only when H$_2$ is added leads to the conclusion that they are caused by the formation of H$_2$Cl$^+$. The chloronium ion (H$_2$Cl$^+$) has been previously documented as a species produced in discharges of HCl and hydrogen [6.1]. Since these peaks are larger than the cracking pattern of SiH$_2$Cl$_2$, it shows conclusively that Cl is being stripped from SiH$_2$Cl$_2$ in the gas phase. There are two possible mechanisms that may perform the stripping, electron impact dissociation and H abstraction of Cl from SiH$_2$Cl$_2$ with ionization. With only SiH$_2$Cl$_2$ and a He plasma (containing He*, He$^+$, and e-) or SiH$_2$Cl$_2$ in the 70eV electron beam of the mass spectrometer HCl, is indeed formed. Since there are no gas phase collisions in the mass spectrometer, the HCl formed is a decomposition product of the reaction,

$$\text{SiH}_2\text{Cl}_2 + X \rightarrow \text{HCl} + \text{(SiHCl or SiHCl}^+ + \text{e})$$

(6.1)

where X is either e-, He* or He$^+$. In fact, the collision cross-section is greatest at electron energies much less than 70 eV [6.2]. Since the relative ion peak intensities for the mono- and di-chlorosilanes are similar when compared with the cracking pattern, an electron impact dissociation mechanism indicated. This might seem counterintuitive with the addition of downstream H$_2$, but any large electron temperature (voltage) decrease is offset by an increase in the electron density (current) in order to maintain constant power. The efficiency of SiH$_2$Cl$_2$ cracking will be proportional to the total number of electrons over the excitation threshold. Any hydrogenation of these species probably occurs afterwards. The hydrogen ionization/hydrogenation mechanism does not appear likely.
H$_2$Cl$^+$ occurs in gaseous discharge systems of H$_2$ and HCl because the attraction of protons to HCl (proton affinity 6.1 eV) is greater than attraction to H$_2$ (proton affinity 0 eV) [6.1,6.3]. Due to the dipole of the HCl molecule, it is easy to see that a proton will be attracted to the net negative charge of the chlorine atom. H$_2$ has no dipole moment; hence, it has no affinity for protons; and other protons will be repelled.

There are several possible mechanisms by which H$_2$Cl$^+$ ions participate in the film growth process. For example, they are able to hydrogenate Si on the growing surface to promote etching. Protons are much more reactive than neutral H radicals and H$_2$ molecules, thus promoting hydrogen driven surface reactions. Another possibility is that the proton may be used to "dehalogenate" the surface, to promote crystalline over amorphous growth [6.4]. Just as Si may be bound to a crystal by the proposed reaction, it may be removed by the reverse reaction involving hydrogenation. If the bonds can be hydrogenated before the Si is covered by other silicon groups, then it is possible to remove from the surface. In addition, selectivity may be enhanced by etching of Si species attached to the oxide preferentially to Si species on Si (see Fig. 6.7). It will take less energy for a proton to break the donor/acceptor bond between surface oxygen atoms of the oxide and surface attached Si, than to break the Si-Si bond of crystalline Si.

As stated in Section 6.3, a "wall loading" sequence is required prior to deposition in order to achieve selective film growth under these conditions. When this sequence is not included, conditions under which selective growth can be obtained yield either no film growth or uniform substrate coverage. It appears that residue from the wall loading step is extracted from the surfaces of the chamber to assist growth and etching. However, when the H$_2$ flow rate is less than 5 sccm, a crystalline film is grown uniformly across the sample surface, regardless of wall loading. By using a He/H$_2$ discharge, it is possible to remove all traces of these species; HCl species are depleted first. Since wall loading appears to play a major role, the concentration of the etchant and/or deposition species need
to be increased by increasing the SiH₂Cl₂ concentration in order to minimize the need for wall loading. The 1% concentration of SiH₂Cl₂ in He was used because pure SiH₂Cl₂ has a bottle pressure of 9 psi which is incompatible with the gas control system. Compensation by higher gas flow rates, such as 100 sccm, for such dilute bottles would alter the flow pattern in the reactor in comparison with other deposition chemistries.

6.5 Summary

This chapter has demonstrated the effect of H₂ flow rate on the gas phase species existing in the presence of SiH₂Cl₂ downstream from an rf He discharge. For the first time it has been shown how SiH₂Cl₂ decomposes in a plasma in the presence of H₂ and in the presence of H₂Cl⁺ in a deposition reactor. The SiH₂Cl₂ is stripped of Cl, producing chlorinated silane ions and H₂Cl⁺ ions. The H₂Cl⁺ ion might be an etchant species and the chlorinated silane might be a deposition precursor. SiH₃ in this system is shown to be an etching product. The gas phase hydrogenation of the SiH₂Cl₂ precursors is quite limited. Furthermore, it appears that the dissociation/ionization of SiH₂Cl₂ is caused by an electron impact mechanism.

It has also been shown that this process can produce selectively grown crystalline Si films at 300°C. The low deposition rates and sensitivity of the process to wall conditions suggests that the process is in an almost equilibrium state between net etching and deposition of films. Therefore it is important to study the kinetics of etching and deposition reactions so that the process may be altered accordingly.

This work also raises several research issues. What is the effect of the Si:Cl ratio on the selectivity and deposition? How do halogens affect the surface reactions? Since H₂Cl⁺ is present, and it is known to be a super-acid, how would fluorine substitution affect the degree of selectivity? How will increasing the Si and Cl precursors in the gas phase affect the process?
7 Silicon Nitride Growth

This chapter discusses the effects of 1) additions of other-element source gases (NH\textsubscript{3} and N\textsubscript{2}) and 2) plasma excitation frequency on silicon nitride films grown by the remote PECVD process. The use of different sources gases and excitation frequency can produce dramatic changes in the growth rate and in the bonded hydrogen groups in nitride films. There is considerable interest in the use of microwave, as well as radio-frequency excitation for remote plasma reactors. Direct comparisons are required to explain differences in precursor formation, reaction pathways, and film properties. The remote PECVD process permits a study of the deposition process chemistry in ways that are not possible using conventional PECVD because of geometrical constraints. For example, it is simple to change the powered electrode for remote PECVD so that studies of different power coupling methods may be made with the same chamber geometry.

7.1 Objectives

As shown in chapter 4, the excitation frequency directly affects the electron concentration in the reactor. In turn this frequency dependence affects the a-Si:H codeposition reaction rate in oxide and nitride deposition. Also, deposition reactions can be initiated through excitations of silane by neutral radical species, such as atomic hydrogen. Such excitation of course depends on the presence of the radical precursor, i.e., NH\textsubscript{3} is a source of hydrogen, while N\textsubscript{2} is not. Therefore, the objectives of this chapter are to determine precursors for nitride growth and to determine under what conditions exist. In addition, the mechanisms by which these precursors initiate deposition reactions are discussed. The ir properties of nitride films will be presented to demonstrate the bonded hydrogen configurations in the films, and how they differ depending on the deposition technique.

7.2 Approach

In order to show the effects of the deposition mechanisms, films are grown with either 13.56 MHz or 2.54 GHz excitation frequency, and with either N\textsubscript{2} or NH\textsubscript{3} as
nitrogen source-gas precursors. Films are grown at several positions for each combination. Mass spectrometry of neutral species is measured for these conditions at the 2.54 cm position. Infrared measurements are used to determine the NH and SiH content of the films in order to demonstrate how deposition conditions affect film microstructure. The SiH concentration, measured through ir absorption in the films, is shown as a function of disilane concentration, measured by mass spectrometry. It demonstrates the relationship between a-Si:H codeposition reaction and film growth. In addition, the NH concentration is plotted as a function of SiN(s) peak position for both films grown with N\textsubscript{2} and NH\textsubscript{3} nitrogen source gases.

The default growth conditions are, 300 mTorr pressure, 200 sccm total flow of gas through the plasma tube: a mixture of He, and either N\textsubscript{2} or NH\textsubscript{3}, and 10 sccm flow of 10\% SiH\textsubscript{4} in He injected downstream. All samples are grown at 140°C so the films retain bonded hydrogen in either SiH and/or SiNH groups. The applied power is 25 W for the rf plasma and 170 W for the microwave plasma. The high power required for microwave discharges is the minimum power at which the plasma is stable. Mass spectrometric results are used to examine the neutral fragmentation patterns of chamber generated species. The plasma applicators described in Chapter 2 are both used in this study. The Langmuir probe position is measured from the base of the exposed probe tips.

7.3 Results

7.3.1 Nitride deposition

Figure 7.1 is an ir absorption plot displaying the features of a hydrogenated silicon nitride film. The NH stretching, NH(s), and NH bending, NH(b), bands are shown at 3350 and 1175 cm\textsuperscript{-1}, respectively, and the NH\textsubscript{2} scissors bending mode at 1550 cm\textsuperscript{-1} [7.1]. The SiN bonds have a stretching feature, SiN(s), located between 820-890 cm\textsuperscript{-1}.

The deposition rate with respect to position from the end of the plasma tube is shown in Figs. 7.2 for both N\textsubscript{2}/He and NH\textsubscript{3}/He discharges. The plasma power is 25 W at
Figure 7.1- Infrared absorption spectrum of a heavily hydrogenated silicon nitride film.
Figure 7.2- Deposition rate as a function of growth position for N2 and NH3 N-source gases at 50 sccm and 150 sccm He in the plasma tube, 10 sccm 10% SiH4 + He, and 300 mTorr, at 13.56 MHz, 25W, and 2.54 GHz 170W. The lines are meant as a guide to the reader.
13.56 MHz and 170 W at 2.54 GHz. The plasma tube flow rates are: 150 sccm He with
50 sccm of either N$_2$ or NH$_3$ injected through the plasma-excitation tube. The highest
deposition rates always occur closest to the plasma tube and reach deposition negligible
rates 40 cm downstream from the plasma generation region. With rf excitation the
deposition rates are comparable for the two N-atom source gases at the 5 cm position. The
deposition rate ratios remain within a factor of 3 at distances less than 12 cm. However,
the deposition rate using the N$_2$ source gas drops more rapidly than when using the NH$_3$
source gas. There is no detectable deposition beyond 14 cm downstream with the N$_2$
source gas, whereas the deposition rate only falls by 50% with NH$_3$.

The deposition rates using microwave excitation are very different from those using
rf excitation (Fig. 7.2). The deposition rate for the 2.54 GHz NH$_3$/He discharge is 2 times
higher than the deposition rate for the 13.56 MHz discharge at the 3 cm position. For
N$_2$/He mixtures, the microwave excitation has a deposition rate 140 times lower compared
with the rf discharge at 3 cm downstream. In addition, it is observed that no film can be
grown using microwave discharges of pure He. Deposition of a film using the 2.54 GHz
microwave source requires excitation of either N$_2$ or NH$_3$. Film growth is several hundred
times faster with NH$_3$ than with N$_2$ as the source gas.

Figure 7.3 shows the bonded hydrogen content as a function of position from the
end of the plasma tube for 13.56 MHz discharges. The concentrations were determined
from the analysis of ir absorption data in the bond-stretching frequency regimes of 2000-
2200 cm$^{-1}$ for SiH and 3000-3500 cm$^{-1}$ for Si-NH. For films grown near the plasma tube
(2.5 cm downstream), the total bonded hydrogen concentrations are within a factor of two
for films grown at 13.56 MHz using the both source gas mixtures, 2.3 x 10$^{22}$ cm$^{-3}$ for the
N$_2$ mixture, and 4.0 x 10$^{22}$ cm$^{-3}$ for the NH$_3$ mixture. However the Si-H groups dominate
in films grown with the N$_2$ source gas and NH groups dominate when the NH$_3$ source gas
is used. Moreover, there is virtually no detectable SiH in the films deposited from the NH$_3$
source gas mixture, while there are trace amounts of NH in the films grown using the N$_2$
source case mixture. At all deposition positions the films deposited using the NH$_3$ source
Figure 7.3- Hydrogen content (N-H and Si-H groups) as a function of growth position for N2 and NH3 N-source gases at 50 sccm and 150 sccm He in the plasma tube, 10 sccm 10% SiH4 + He, and 300 mTorr, 13.56 MHz, 25W. The lines are meant to guide the reader.
gas contain more bonded hydrogen. However, the H concentration decreases with increasing position (and deposition rate) for both N\textsubscript{2} and NH\textsubscript{3} source gases.

Bonded hydrogen could not be detected in the films produced by microwave excitation of N\textsubscript{2}/He source gases because the films were too thin. The bonded hydrogen of films grown by microwave excitation of NH\textsubscript{3}/He mixtures shows both SiH and NH bonding. For 50 sccm of NH\textsubscript{3}, the [Si-NH]/[SiH] ratio is about 3 for plasma excitation using the 2.54 GHz microwave discharge, whereas this ratio is more than 100 using the same gas flows and 13.56 MHz rf excitation.

Figure 7.4a shows the deposition rate as a function of both N-atom source gas flow rates at 13 cm downstream for 13.56 MHz excitation and of the NH\textsubscript{3} flow rate for 2.54 GHz excitation for the 2.5 cm downstream growth position. Using 13.56 MHz excitation and the N\textsubscript{2}/He mixture the deposition rate changes very little, averaging about 2 Å/min over the entire range of N\textsubscript{2} flow rates (10 sccm to 100 sccm). The NH\textsubscript{3} process using 13.56 MHz excitation shows a linear increase in deposition rate with NH\textsubscript{3} flow rate up to about 30 sccm NH\textsubscript{3}. It shows saturation in growth rate of \(\sim\)50 Å/minute for flow rates between about 30 sccm and 100 sccm. The deposition rate for the 2.54 GHz excitation of NH\textsubscript{3}/He discharges is measured at 2.54 cm downstream from the plasma tube, and shows deposition rates as high as 200 Å/m. At 13 cm downstream, however, the deposition rate is negligible at 50 sccm NH\textsubscript{3}.

Figure 7.4b shows the bonded hydrogen concentrations of NH and SiH as a function of the NH\textsubscript{3} flow rate for 2.54 GHz excitation. At the lowest flow rates, 1 to 2 sccm NH\textsubscript{3}, the bonded hydrogen is present almost entirely as NH. As the flow rate increases, the NH concentration decreases in a super-linear manner between 1 sccm and 30 sccm, and then saturates off between 30 sccm and 50 sccm. The NH concentration ranges from \(4 \times 10^{22}\) cm\(^{-3}\) to \(2 \times 10^{22}\) cm\(^{-3}\). The bonded H concentration of SiH groups behaves oppositely, ranging from not detectable to \(5 \times 10^{21}\) cm\(^{-3}\). This behavior is different for the bonded hydrogen in films grown from 13.56 MHz discharges and NH\textsubscript{3}/He mixtures. Depositions with NH\textsubscript{3} <1\% resulted in films in which the SiH groups dominate hydrogen
Figure 7.4- a) Deposition rate of silicon nitride films as a function of NH$_3$ flow rate, Power is 25W at 13.56 MHz, and 170W at 2.54 GHz, b) Hydrogen concentration in silicon nitride films as a function of NH$_3$ flow rate, Power is 25W at 13.56 MHz. The lines are meant to guide the reader.
incorporation. At higher flow rate ratios of NH₃ to He, NH groups dominate. For 13.56 MHz rf excitation of N₂/He mixtures, the incorporation of hydrogen is dominated by SiH bonding groups at all flow rate ratios, the Si-NH concentration is below ir detectable limits.

Figure 7.5 shows the fraction of silicon-bonded H in SiH bonded groups to the total bonded hydrogen concentration as a function of the NH₃ gas flow rate for the two excitation frequencies. For 13.56 MHz rf excitation, the fraction of SiH groups drops from 80% to about 5%, as the NH₃ flow rate increases from about 2.5 sccm to 20 sccm. In contrast, the fraction of SiH groups in the films produced by 2.54 GHz microwave excitation increased with increasing NH₃ flow, approaching a saturation value of approximately 30% for NH₃ flow rates between 30 and 50 sccm.

7.3.2 Discharge Composition

7.3.2.1 N₂/He Atmosphere

Figure 7.6 shows the effect of N₂ flow rate on the 14 m/z signal from the mass spectrometer for the N₂/He discharges at 13.56 MHz and 2.54 GHz, 10 sccm 10% SiH₄ + He injected downstream, and the mass spectrometer positioned 2.54 cm downstream. The four traces show the magnitude of mass 14 for 0 W and 25 W at 13.56 MHz, and at 0 W and 170 W at 2.54 GHz. The 2.54 GHz curves are multiplied by a factor of 2. The behavior of each trace is linear with respect to the N₂ flow rate. The trace for the 13.56 MHz discharge shows a 40% decrease of mass 14 when SiH₄ is injected downstream and the rf power is 25 W. However, no measurable change between the 0 W and 25 W rf excitations was detected when the SiH₄ flow was reduced to zero. For the 2.54 GHz discharges, the change in mass 14 for the power levels of 0 W and 170 W is within the noise limit for detection, ~1%. The mass 14 signals for discharges of both frequencies are attributed to N₂. No Si-N precursors, e.g., silamines, were formed. In addition: no polysilane, Si₃H₇ mass features were detected under any conditions, and there were no significant changes in the hydrogen signals, whether or not SiH₄ was flowing.
Figure 7.5- Fraction of hydrogen bonded to Si as a function of NH3 flow rate. 2.54 GHz 170W, 13.56 MHz 25W, 300 mTorr, 10 sccm 10% SiH₄ + He.
Figure 7.6. Mass 14 m/z signal as a function of N2 flow rate for 13.56 MHz and 2.54 GHz, 300 mTorr, 200 sccm total plasma gas flow rate of N2 and He, 10% SiH4 + He.
7.3.2.2 NH₃/He atmosphere

Figures 7.7a and 7.7b display the mass spectrometer signals for masses 14 and 15, and masses 16 and 17, respectively, as a function of the NH₃ flow rate for 13.56 MHz discharges with 10 sccm 10% SiH₄ + He injected downstream. Mass 14 corresponds to N⁺, mass 15 to NH⁺, mass 16 to NH₂⁺ and mass 17 to NH₃⁺. Corrections are made for background gases such as O, mass 16, and OH, mass 17, etc. whenever necessary. Figures 7.7a and 7.7b show that the mass spectrometer signals remain linear with respect to flow rate fro masses 14-17 when the rf power is 25 W. Mass 14 shows a 20% decrease and mass 15 shows a 25% decrease, compared to a 35% decrease for masses 16 and 17.

For the 2.54 GHz discharges, the traces in Fig. 7.8 for masses 14 and 15 display increases when microwave power increases from 0 W to 170 W. The intensities of masses 15, 16 and 17 (16 and 17 are not shown) increase superlinearly with increased NH₃ flow, but remain proportional to one another. However, the mass 14 trace shows signal saturation at flow rates above 30 sccm NH₃. Comparisons of changes in mass 14 with NH₃ flow to changes in masses 28, N₂, and 17, NH₃, show that mass 14 derives almost entirely from these species; at most 5% could come from other species. It should be noted that 3 to 4 times more hydrogen is produced in the 2.54 GHz discharges than in the 13.56 MHz discharges, and that the film deposition rate shown in Fig. 7.4 tracks the production of H.

7.3.3 Film Properties

Figure 7.9 shows the effect of [NH] content on the SiN(s) peak position. The plot contains data from films grown with both N₂/He and NH₃/He discharges. It displays a positive correlation with the SiN(s) peak position at 830 cm⁻¹ at low N-H concentrations, while for [NH] at 5 x 10²² cm⁻³ (~30% bonded hydrogen), the SiN(s) peak position is around 890 cm⁻¹. This relation is similar to behavior shown by D. V. Tsu [7.2,7.3]. However, Fig 7.9 also shows that the behavior is independent of the N-source gas.
Figure 7.7- Mass signals as a function of NH$_3$ flow rate for 13.56 MHz. a) 14 and 15 m/z, b) 16 and 17 m/z. 300 mTorr, 200 sccm total plasma tube gas flow rate of N$_2$ and He, 10 sccm 10% SiH$_4$ + He.
Figure 7.8- Mass signals as a function of NH$_3$ flow rate for 2.54 GHz. a) 14 and 15 m/z, b) 16 and 17 m/z. 300 mTorr, 200 sccm total plasma tube gas flow rate of N$_2$ and He, 10 sccm 10% SiH$_4$ + He.
Figure 7.9- SiN(s) band position as a function of N-H concentration in silicon nitride films.
The relation of NH(s) and SiN(s) band positions are shown in Fig. 7.10. The plot compares the maxima of the two bands and shows that there is a strong correlation between the two peaks for SiN(s) frequencies below 870 cm\(^{-1}\), with a linear regression fit of 0.987. The data was collected from films of NH\(_3\)/He discharges for different growth positions, power levels, and NH\(_3\) flow rates.

Figure 7.11 compares mass spectrometry signals of silane and disilane species with [SiH] in nitride films deposited by NH\(_3\)/He and N\(_2\)/He discharges. The masses selected represent the silane source components (mass 31) and the higher molecular weight silane species (mass 60), and were chosen for their relative signal strength. The plot shows that as [SiH] concentration increases, the mass 31 signal decreases linearly and mass 60 signal increases linearly.

7.4 Discussion

7.4.1 Deposition Mechanisms

This study has shown that a-Si:H films cannot be deposited by pure He microwave-driven discharges, while silicon nitride can be deposited only with low deposition rates using N\(_2\)/He mixtures. This means that any non-charged active He or N species, e.g., He metastables, N-atoms, or ions, transported out of the plasma into the chamber do not promote measurable film deposition. In contrast, silicon nitride films have been deposited using rf-excitation of N\(_2\)/He source gas mixtures. Infrared studies have shown that these films can contain bonded hydrogen in both SiH and Si-NH configurations (Fig. 7.2). Films deposited between the first dispersal ring and the plasma tube have both bonded hydrogen groups, whereas SiH is the dominant bonded configuration in films deposited downstream from the first dispersal ring and the films have subnitride stoichiometry.

Film deposition beyond the first dispersal ring is primarily driven by energetic electrons transported into the chamber under the influence of the electric field associated with the plasma excitation electrode geometry; i.e., the chamber fixtures (gas dispersal
Figure 7.10: NH(s) IR stretching band as a function of SiN(s) IR stretching band in silicon nitride films.
rings and chamber walls) are a ground for accelerating electrons downstream (Figs. 3.4 and 3.3). In the region between the dispersal ring and the plasma tube, SiH4 injected downstream can diffuse back to the mouth of the excitation tube and be fragmented by energetic electrons. This process produces atomic hydrogen which drives a deposition reaction that incorporates H-atoms in both SiH and Si-NH bonding configurations. This mechanism is supported by this study of deposition from NH3/He plasmas, and by the previously reported studies of Johnson et al. [7.4,7.5].

The data in Fig. 7.5 show that the distribution of bonded hydrogen between SiH and Si-NH groups is different for films deposited by 13.56 MHz and 2.54 GHz excitation of NH3/He discharges. The nitride deposition process for low NH3 flow rates involves two SiH4 and N-atom source gas activation mechanisms, the creation of H and NH groups in the plasma as detected by mass spectrometry, and the break-up of SiH4 by energetic electrons extracted from the plasma. At higher NH3 flow rates, the process involves deposition reactions driven by the H and NH groups generated within the plasma region. This proposed mechanism for film growth reactions is consistent with the previously reported studies of sub-oxide deposition, in which two parallel mechanisms dominated in the sub-oxide deposition region: 1) deposition of an a-Si:H alloy component with SiH bonds that derived from electrons exciting the SiH4 reactant, and 2) deposition of an SiO2 component that derived from active O-species reacting heterogeneously at the substrate with the SiH4 [7.6,7.7].

The distribution of bonded H between SiH and Si-NH in the nitride films deposited using 2.54 GHz excitation of NH3/He source gas mixtures is qualitatively different as displayed in Figs. 7.5,7.3,7.4b. Films deposited at the lowest NH3 flow rates can be driven by H and NH species extracted from the plasma. The absence of SiH groups in these films and the lack of gas phase Si-N species suggest that these species react with SiH4 at the substrate and produce nitride films with Si-NH groups. It is the same
neighboring NH groups decreases. The decrease in distance lowers the mean frequency of the NH(s) absorption band due to hydrogen bonding [7.9]. The range of band positions from 3365 to 3330 cm\(^{-1}\) corresponds to N···N spacings of 3.10 to 3.09 Å. Once the NH concentration has reached a point where the SiN(s) peak has shifted to 870 cm\(^{-1}\), it appears that NH groups no longer affect the stretching vibration; i.e., the NH(s) peak does not shift past 3330 cm\(^{-1}\). Therefore, increasing the NH concentration increases the SiN bond angle through relaxation. Thus it raises the SiN(s) stretching frequency, reduces the mean NH group spacing, and lowers the NH(s) stretching frequency.

The plot in Fig. 7.11 shows how the SiH incorporation in the films changes as a function of silane flow rate. The plot demonstrates that the incorporation of SiH, hence Si-Si bonds, is a function of the disilane concentration and is independent of the N-source gas. The fact that the mass 60 signal has the same behavior for both N\(_2\)/He and NH\(_3\)/He 13.56 MHz discharges, demonstrates that polysilane formation is not affected by the type of N-source gas injected into the reactor. The implication is that the chemistry that promotes SiH group formation in the nitride films is independent of the gas discharge sources, i.e., it is likely to be driven by e-.

Since NH bond formation appears to occur during deposition, the ratio of NH\(_3\) to SiH\(_4\) might affect the microstructure. It is quite likely that the films grown with NH\(_3\)/He discharges utilize Si(NH\(_2\))\(_x\) species formed in the gas phase or the surfaces are saturated with NH groups. Smith et al. showed that aminosilanes are key to nitride growth in glow discharge processes [7.10]. However, the geometry of the mass spectrometer sniffer tube impedes the collection of these species. With 10 sccm NH\(_3\) flow rates (at 300 mTorr), the entire film surface is bombarded with NH\(_3\) once every 60 msec. Since the samples were all grown at 140°C, it is relatively unlikely that much NH is incorporated into the films by a post-deposition process, such as NH\(_3\) condensation and diffusion upon cooling. As will
The study showed that NH incorporation helps relax the network since SiN(s) wavenumbers increases with increasing [NH]. There is a direct relation between [NH] and the NH(s) band position. The dipole effect of neighboring N-H groups modifies the force constant of the NH bond thus shifting the band maxima to slightly lower wavenumbers. This average N-H...N distance for neighboring N-H groups varies from 3.10 to 3.09 Å for 3365 to 3330 cm\(^{-1}\). Finally, it is speculated that NH incorporation in films grown with NH\(_3\)/He discharges occurs during growth due to the high NH\(_3\) partial pressure in the reactor.

References


8 Silicon Oxide Growth

Because the gas phase chemistry of SiO₂ deposition by remote PECVD has been well characterized [8.1-8.3], the reaction system is a good candidate for a detailed study of how reaction by-products can affect film properties. Tsu has shown that the OH content of SiO₂ films can be controlled by adjusting process parameters such as SiH₄/O₂ ratio and substrate temperature [8.3]. However, it has been also shown that OH can be incorporated after deposition. Two issues are addressed in this chapter, 1) how is OH incorporated in the films, and 2) what are the changes in film microstructure associated with OH incorporation. The following topics are examined: 1) the nature of the incorporation mechanisms, 2) the Si-O network changes upon accommodation of OH, 3) the local environment in which the OH groups exist within the film, and 4) the source of the 925 cm⁻¹ ir absorption band [8.4,8.5]. From an engineering standpoint, the goal is to produce films that have minimal OH incorporation and that are not susceptible to post-deposition OH incorporation.

8.1 Objectives

One purpose of this chapter is to show whether the differences in OH incorporation result from intrinsic or extrinsic processes. By placing a-Si:H diffusion barriers over the oxide films at different points in film processing, it is possible to isolate the time at which OH is incorporated. There are three times in the processing of SiO₂ films in which OH may be incorporated: 1) during oxide deposition, 2) after film deposition, while the film remains in the deposition chamber under a relativity high vacuum, and 3) after the film has been removed from the chamber. Incorporation during deposition means that the mechanism is intrinsic to the deposition process reaction pathways, whereas incorporation after deposition means that the mechanism is not a direct function of the film growth process reactions.
When OH is incorporated into the oxide, the film can undergo changes in its local atomic structure. As will be shown, incorporation occurs through preferential reaction with Si-O-Si bonds with bond-angles of the low side of the bond angle distribution; these bonds are highly strained and are therefore highly reactive. This preference for bond angles on the low side of the distribution means that the distribution of bond angles shifts, implying that network relaxation might occur during the incorporation of OH groups. Changes in the microstructure can affect the internal film stresses, the dielectric film properties, and the films susceptibility to impurity incorporation.

The local environment in which OH groups are incorporated will also be discussed. As mentioned in subsection 2.2.3.1.3, it is understood that the spacing of neighboring OH groups modifies the OH bond-stretching vibrational frequency, OH(s). Therefore, changes noted in the OH(s) band shape are correlated to changes in the distribution of local environments of the OH groups. By examining the OH(s) band in detail, it is possible to identify what those local environments are. It will be shown that neighboring OH groups contribute to an ir absorption band at 925 cm\(^{-1}\). The occurrence of this band coupled with other spectral changes provides a basis for defining local atomic arrangements of Si-OH groups and the particular hydrogen-bonding reactions that are local environment dependent.

It is important to create OH free films to produce materials with high dielectric breakdown and low leakage current. In order to understand why certain oxide films are susceptible to OH incorporation, it is important to understand the behavior of hygroscopic SiO\(_2\) films. Such an understanding will reveal: 1) how to \textit{immunize} these films against OH incorporation, and 2) how to create films not prone to OH incorporation. Therefore, data on OH incorporation methods is presented, and the methods by which OH may be prevented from entering oxide films are discussed.
8.2 Approach

A series of experiments was performed to determine whether silanol (SiOH) groups are incorporated via an intrinsic or extrinsic mechanism (see Table 8.1). To accomplish this, a-Si:H diffusion barriers were deposited after the deposition of SiO₂ films to prevent post-deposition OH formation that could result from reactions with ambient water. First, a series of SiO₂ films was deposited and capped immediately after deposition to eliminate any post-deposition incorporation processes which could occur in the chamber during cool-down or outside the vacuum system in the laboratory ambient, (approximately 50% RH and 75°F). Next, a series of SiO₂ films was capped, but after permitting exposure of the oxide layer to the chamber ambient for roughly 30 minutes at a pressure 0.3 Torr. These experiments were performed to determine if OH formation associated with wall contamination during deposition, etc., can occur during sample cool-down in the deposition chamber. Finally, SiO₂ films were deposited without any capping to determine the effects of exposure to: (a) moist laboratory air, and (b) different in-situ processing steps via intrinsic mechanisms related to the deposition reaction process pathways.

Table 8.1- Summary of Deposition Conditions for OH Incorporation Source Experiments. During the oxide deposition, the grid was allowed to float to the plasma potential. To deposit the a-Si:H diffusion barrier, the following conditions were maintained: Tₜ 200°C, He flow 100 sccm, 10% SiH₄ + Ar flow 10 sccm, rf Power 31 W, the grid was grounded to the chamber potential.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tₜ (°C)</th>
<th>rf Pwr (W)</th>
<th>He flow (sccm)</th>
<th>O₂ flow (sccm)</th>
<th>10% SiH₄ + Ar flow (sccm)</th>
<th>Dep. Time (min)</th>
<th>Capping Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOY10</td>
<td>200</td>
<td>12</td>
<td>80</td>
<td>N₂O 20</td>
<td>10</td>
<td>15</td>
<td>Immediate</td>
</tr>
<tr>
<td>AOX92</td>
<td>200</td>
<td>16</td>
<td>90</td>
<td>O₂ 10</td>
<td>5</td>
<td>15</td>
<td>Immediate</td>
</tr>
<tr>
<td>AOX94</td>
<td>200</td>
<td>17</td>
<td>90</td>
<td>O₂ 10</td>
<td>5</td>
<td>15</td>
<td>Held @ 200°C</td>
</tr>
<tr>
<td>AOY07</td>
<td>200</td>
<td>12</td>
<td>80</td>
<td>O₂ 20</td>
<td>10</td>
<td>20</td>
<td>Cooled to 81°C</td>
</tr>
<tr>
<td>AOX89</td>
<td>250</td>
<td>18</td>
<td>90</td>
<td>O₂ 10</td>
<td>5</td>
<td>21</td>
<td>None</td>
</tr>
<tr>
<td>AOY42</td>
<td>200</td>
<td>13</td>
<td>90</td>
<td>O₂ 10</td>
<td>10</td>
<td>4</td>
<td>None</td>
</tr>
</tbody>
</table>
Two samples, AOY42 and AOX89, were studied in greater detail to examine how SiOH formed in them over time and to determine how the SiO(s) band changes position and shape during SiOH formation. The deposition conditions for these films are listed in Table 8.1. Sample AOY42 was monitored by ir, seven times in the first 36 hours. A final ir measurement was made three weeks after deposition. The ir spectrum was taken for sample AOX89, daily for the first five days. This sample was then subjected to a deionized (D.I.) water boil for 30 minutes after which another ir spectrum was obtained. Three weeks later the same sample was furnace annealed and another scan was made immediately after this anneal; a final scan was made 90 days later.

To produce the SiO$_2$ films, a mixture of 10-20% O$_2$, or N$_2$O, and He at a total flow rate of 100 sccm, is rf excited (8 to 17W), with the chamber pressure maintained at 300 mTorr during deposition. The reactor used for this study is the 5.2 cm diameter chamber. A mixture of 10% SiH$_4$ + Ar is injected through the first gas dispersal ring at a rate of 5 to 10 sccm. The SiH$_4$ is not in direct contact with the plasma after-glow since the grid is in its floating bias mode. The substrate is positioned at the first station downstream from the first gas ring. The substrate (100) n-type Si, 10-70 Ω-cm) is typically heated to a temperature (T$_s$) of 100 to 250°C.

To produce the 800Å to 900Å thick a-Si:H encapsulating layer, the following operations are performed sequentially: the oxygen source is switched off, the rf power is increased to 32W, and the bias state of the grid is switched to the grounded mode. For a-Si:H deposition, the grid is grounded; whereas for oxide deposition, it is floating to prevent excitation of the silane and consequent formation of hydrogenated suboxides.

8.3 Results

8.3.1 Infrared Spectra

Figure 8.1 shows representative ir absorption spectra for samples deposited by remote PECVD at substrate temperatures of 100 and 200°C. The 200°C spectrum shows
features at 1060 cm\(^{-1}\), 810 cm\(^{-1}\), 445 cm\(^{-1}\), corresponding respectively to stretching (s), bending (b), and rocking (r) motions of the oxygen atom relative to its two silicon neighbors. The absence of a feature at 3600 cm\(^{-1}\), the OH(s) band, indicates that the Si-OH concentration is below detectable limits, < 10\(^{19}\) cm\(^{-3}\). The 100°C ir spectrum shows essentially the same Si-O features as the 200°C sample, but with an additional weak absorption at 3600 cm\(^{-1}\) that indicates the presence of Si-OH groups. The other small changes in the Si-O features are discussed in detail below.

Figure 8.2 shows a typical spectrum for a film deposited for this study (sample AOX89), and shows all of the Si-O features. Note that the SiO(s) spectral peak is at a higher wavenumber than it is in Fig. 8.1 (1064 cm\(^{-1}\), rather than 1050-1055 cm\(^{-1}\)) and that the full-width at half-maximum (FWHM) is 82.3 cm\(^{-1}\) rather than in excess of 90 cm\(^{-1}\). The internal O-H bond-stretching feature of the Si-OH group in the vicinity of 3600 cm\(^{-1}\) is evident. This band is asymmetric with a sharp spectral cut-off, about 50 cm\(^{-1}\) above the band peak, on the high wavenumber side and about 200 cm\(^{-1}\) below the spectral peak on the low wavenumber side. There also appears to be a broad symmetric feature superimposed on the asymmetric feature, centered around 3350 cm\(^{-1}\). There is an additional absorption feature at approximately 925 cm\(^{-1}\). There is no evidence for bands at either 2260 cm\(^{-1}\) or 875 cm\(^{-1}\); these are the positions of the spectral features associated with the bond-stretching and bond-bending vibrations, respectively, of Si-H groups in an SiO\(_2\) host network [8.6].

### 8.3.2 Capped Oxide Experiments

Several films were encapsulated with a-Si:H at different stages of processing. The spectra for two films deposited at 200°C that were capped immediately following deposition are shown in Fig. 8.3. The distorted baselines in these spectra are caused by interference fringes characteristic of the a-Si:H/SiO\(_2\)/c-Si composite thin film structure. The absorption band at 635 cm\(^{-1}\) is associated with the SiH bending vibration of the a-Si:H cap.
Figure 8.1- Infrared absorption spectrum of silicon oxides deposited at 100 and 200°C.
Figure 8.2: Infrared absorption spectrum of a silicon dioxide film with high concentrations of OH.
Figure 8.3 - The IR spectra for two films deposited at 200°C with a-Si:H encapsulating layer grown immediately after oxide deposition. N₂O and O₂ was used for O-source gas.
Both spectra in Fig. 8.3 clearly show the three normal vibrational modes of the Si-O-Si group at 1060, 810, and 445 cm$^{-1}$. These spectra show no ir evidence of OH incorporation and demonstrate that even under the deposition conditions of high oxygen concentration in He (10 to 20 % $O_2$ or $N_2O$ in He) used to produce these films, it is possible to produce SiO$_2$ films containing no OH. Therefore, an intrinsic OH incorporation pathway is not observed; i.e., OH formation does not occur during deposition.

Figure 8.4 shows the ir spectra characteristic of two different samples made by delaying the capping procedure. The sample that was held at 200°C during the delay periods, AOX94, displays no OH feature that can be detected via ir, while the sample that cooled to 81°C, AOY07, displays a readily detectable OH feature. The absorption band due to the internal O-H stretching vibration, OH(s), for sample AOY07 is asymmetric, with a peak at about 3650 cm$^{-1}$. Table 8.2 shows the peak positions and the full width at half maximum absorbance (FWHM) for these two films in which capping was delayed under different conditions. The film held at 81°C prior to capping has a SiO(s) band spectral peak with a higher wavenumber than that of the film held at 200°C. This is consistent with the observations made on uncapped films whose spectral peak positions increase with increasing OH incorporation.

Table 8.2- Comparison of Delayed Capped Oxide Films. FWHM is the abbreviation for the full width half maximum of the band.

<table>
<thead>
<tr>
<th></th>
<th>Held at 200°C</th>
<th>Cooled to 81°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(s) Band</td>
<td>1046 cm$^{-1}$</td>
<td>1060 cm$^{-1}$</td>
</tr>
<tr>
<td>OH(s) Band</td>
<td>Not Detectable</td>
<td>3663 cm$^{-1}$</td>
</tr>
<tr>
<td>SiO(s) FWHM</td>
<td>92.6 cm$^{-1}$</td>
<td>101.0 cm$^{-1}$</td>
</tr>
</tbody>
</table>
Figure 8.4 - The ir spectra for two films deposited at 200°C with a-Si-H encasulating layer. a- layer was deposited after a 20 minute hold at 200°C, b- was deposited after cooling for 20 minutes and reaching a temperature of 81°C.
8.3.3 Long Term Monitoring of Oxides

Fig. 8.5a shows the ir spectra for the SiO₂ film, AOY42, in the low wavenumber region, 1400 to 400 cm⁻¹, while Fig. 8.5b shows the spectra in the vicinity of the 1060 cm⁻¹ band, from 1275 to 950 cm⁻¹. Figure 8.5a demonstrates changes in the SiO(s) band with increasing atmospheric exposure. Figure 8.5b shows generation of Si-OH groups resulting from reactions with atmospheric water vapor. In Fig. 8.5a, the spectral peak of the SiO(s) band shifts from the as-deposited value of 1050 cm⁻¹ to 1065 cm⁻¹ upon exposure to atmospheric water. The SiO(s) peak positions for all oxide samples produced in this study range from 1042 cm⁻¹ for as-deposited spectroscopically Si-OH free samples, to 1072 cm⁻¹ for films after prolonged atmospheric water vapor exposure. Fig. 8.5b shows that the FWHM decreases significantly, from the as deposited value of 82 cm⁻¹, to the prolonged exposure value of 68 cm⁻¹. The range of FWHM is from an as-deposited value of 92 cm⁻¹ to 66 cm⁻¹. For comparison, fully-relaxed thermal oxides have average spectral peak positions of 1078 cm⁻¹ ±1 cm⁻¹, with FWHM ranging between 74 cm⁻¹ and 76 cm⁻¹. The majority of these changes occur within 10 hours of removal of the sample from the chamber, though changes could be detected up to three weeks after film deposition. The integrated absorbance at the spectral peak ultimately increases as the position and FWHM shift, from the as-deposited value of 16600 cm⁻¹ to 19800 cm⁻¹, after the prolonged exposure. Although not demonstrated by the sample in Fig. 8.5b, the high-wavenumber shoulder of the SiO(s) band has been observed to increase in amplitude relative to the SiO(s) peak height.[8.4,8.5]

The OH incorporation in the film is accompanied by the appearance of the OH(s) band centered at approximately 3550 cm⁻¹ as shown in Fig. 8.6. Initially, an asymmetrically shaped OH(s) band appears with a peak at about 3650 cm⁻¹. The OH that produces the asymmetric feature developed either after film growth but before removal from the chamber or after removing the sample from the deposition chamber. The time
Figure 8.5- Infrared spectra for the SiO2 film measured at different times after deposition. Low wavenumber region, a) 3800 to 2800 cm\(^{-1}\), b) 1400 to 400 cm\(^{-1}\).
Figure 8.6 - OH(s) ir band for the SiO2 film measured at different times after deposition. a) OH(s) band centered about 3650 cm⁻¹, b) 3350 cm⁻¹ component of the OH(s) measured at different times. The ordinate is photon wavenumber in units of cm⁻¹.
interval between sample removal and initiation of the IR spectrum is on the order of minutes. The growth of a second symmetric feature, centered at about 3350 cm\(^{-1}\), is evident in the traces labeled 2 days or longer; it increases in relative intensity on a time scale on the order of days and is clearly associated with exposure to atmospheric moisture. In other words, an extrinsic OH source is water vapor in the air and the growth of this symmetric band is a spectroscopic hallmark of its incorporation into the oxide film. Figure 8.7 uses data from Fig. 8.6 to show changes in the peak position and FWHM for the SiO(s) band as a function of time. The FWHM decreases from 82 to 68 in a span of two days, while the peak position shifts from 1050 to 1063 cm\(^{-1}\).

Along with the growth of the OH(s) band, there is also the formation of a new feature at about 925 cm\(^{-1}\) which is assigned to the SiOH group. This discrete band is not detected when only the asymmetric OH(s) feature is present; however, the region between the SiO(s) and SiO(b) features, between 900 and 1000 cm\(^{-1}\), displays a slight shoulder on the SiO(s) band when the asymmetrically shaped OH(s) band is present (Figs. 8.1a and b, spectra (i)). The FWHM of the OH (s) band increases from 372 cm\(^{-1}\) to a maximum width of 425 cm\(^{-1}\) after two days, then ceases to increase. The discrete 925 cm\(^{-1}\) feature appears only in samples which indicate absorption associated with the internal O-H bond-stretching modes of Si-OH group. Fig. 8.8 is a plot of the integrated absorption of the 925 cm\(^{-1}\) band against the entire OH(s) band, including both the 3600 cm\(^{-1}\) and 3350 cm\(^{-1}\) sub-bands (Fig. 8.7a) and the 3350 cm\(^{-1}\) sub-band only (Fig. 8.7b). This plot shows a linear relationship between the two integrated absorptions. A linear regression analysis provides a fit for both curves with a slope of 6.6 x10\(^{-2}\) and a correlation coefficient of 0.821. The x-intercept for the summation of both sub-bands is approximately 3100 cm\(^{-2}\). The linear relationship is preserved at 3350 cm\(^{-1}\), but the x-intercept is at the origin (x=0). Similar behavior was exhibited by samples deposited under a wide range of gas flow conditions, with the O\(_2\) plasma gas content ranging from 0.5% to 100%.
Figure 8.7- Plot of changes in the a) FWHM and the b) peak position for the SiO(s) band.
Figure 8.8- Plot of integrated absorption of the 925 cm\(^{-1}\) band a) against the entire OH(s) ○ band and the b) □ the 3350 cm\(^{-1}\) sub-band only.
Finally, a boiling experiment and a flash annealing experiment (FA), were performed to determine the effects of various post-deposition treatments on OH incorporation in the remote PECVD oxide films. Six days after it was taken from the chamber, sample AOX89 was immersed in boiling deionized (D.I.) H₂O for 30 minutes. Nine days later, i.e., 15 days after deposition, the ir spectrum of the film was measured again. The film was then flash annealed in vacuum for two minutes (at ~700-800°C). Figure 8.3 contains the ir spectra and Table 8.3 shows how different post-deposition treatments affected the position, amplitude, width, and area of the SiO(s) and OH(s) peaks. Surprisingly, after the boiling treatment, the OH(s) band integrated area decreased, but 9 days later the film had recovered more OH than it lost due to atmospheric exposure. After flash annealing (FA), all traces of OH were removed from the film and the SiO(s) peak position which had increased to 1068 cm⁻¹ then decreased to 1063 cm⁻¹. The film was measured again after 90 days and was still found to be OH free.

<table>
<thead>
<tr>
<th></th>
<th>Just Deposited</th>
<th>5 Days</th>
<th>After D.I. Boil</th>
<th>After 9 Day Hold</th>
<th>After FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(s) Band</td>
<td>1056.5</td>
<td>1064</td>
<td>1068.5</td>
<td>1068</td>
<td>1063</td>
</tr>
<tr>
<td>SiO(s) FWHM</td>
<td>100</td>
<td>80.5</td>
<td>78.7</td>
<td>83.0</td>
<td>94.4</td>
</tr>
<tr>
<td>SiO(s) ΔA</td>
<td>0.2897</td>
<td>0.3034</td>
<td>0.3003</td>
<td>0.2728</td>
<td>0.2800</td>
</tr>
<tr>
<td>OH(s) Band</td>
<td>3650</td>
<td>3613</td>
<td>3634</td>
<td>3657</td>
<td>N/A</td>
</tr>
<tr>
<td>OH(s) INTG</td>
<td>4.3</td>
<td>8.36</td>
<td>6.50</td>
<td>9.18</td>
<td>0</td>
</tr>
<tr>
<td>OH(s) FWHM</td>
<td>370</td>
<td>425.3</td>
<td>416.2</td>
<td>499.5</td>
<td>0</td>
</tr>
<tr>
<td>OH(s) ΔA</td>
<td>0.0154</td>
<td>0.0186</td>
<td>0.0150</td>
<td>0.0158</td>
<td>0</td>
</tr>
</tbody>
</table>
8.4 Discussion

The data presented in the previous section demonstrate how reaction by-products can affect film properties and show the properties of films that are both susceptible and immune to OH incorporation. The results show that OH is incorporated only through extrinsic mechanisms, either from H$_2$O desorbed from the chamber walls that diffuses into a cooled oxide film or from atmospheric moisture once the sample is removed from the chamber. Determining the times in the process at which OH appears in the films is discussed in the first subsection. The second subsection examines changes in the SiO(s) band to show that the OH incorporation permits network relaxation. The third subsection discusses the OH(s) band evolution and discusses how the band shape is a reflection of the distribution of O--O distances. Finally, methods of rendering these oxide films immune OH attack are discussed.

8.4.1 Capped Oxide Experiment Interpretation

The oxides in this study were intentionally deposited under conditions favorable to the incorporation of OH as confirmed by the ir results of Fig. 8.5. However, when oxides are produced under the same conditions, but capped immediately after SiO$_2$ formation by an a-Si:H diffusion barrier, no OH was detected by ir. This was independent whether O$_2$ or N$_2$O was used in the deposition process, and shows that within the detection limits of ir spectroscopy an extrinsic post-deposition pathway rather than an intrinsic pathway to OH incorporation is operative. Moreover, two distinct post-deposition sources have been identified: one is associated with the deposition chamber during sample cool-down, and the other with the absorption of atmospheric moisture.

The incorporation of OH is predominantly an extrinsic process, whether inside or outside of the deposition chamber, but details of the spectral features associated with the OH groups can differ for these two cases. Specifically, incorporation in the chamber leads to an OH(s) band that is highly asymmetric; whereas, incorporation outside the vacuum
-176-
system leads to a symmetric OH(s) band and the appearance of a discrete spectral SiOH feature at about 925 cm\(^{-1}\). These spectral differences are associated with different local bonding environments of the silanol groups, which in turn reflect aspects of the reaction chemistry that lead to their incorporation. Although it is clear that moisture, H\(_2\)O, is the molecular source in the "post-chamber-removal" case, it is not absolutely certain that it is also in the "pre-chamber-removal" case. The mechanism may however involve molecular species, presumably containing OH groups that are derived in part from the H\(_2\)O by-product of deposition reactions that are carried out at high O\(_2\) flow rates. Therefore the following post-growth reactions are proposed for the two incorporation mechanisms:

\[
\begin{align*}
\text{H}_2\text{O} + \text{a-SiOSi} \text{ (strained)} & \rightarrow 2\text{SiOH} \quad (8.4) \\
\text{XOH} + \text{a-SiOSi} \text{ (strained)} & \rightarrow \text{SiOH} + \text{SiOX} \quad (8.5)
\end{align*}
\]

The reaction of (8.4) is shown in Figure 8.11. Incorporation of OH groups is not accompanied by any spectral features related to the presence of SiH bonding groups, which would be readily detected by the bond stretching and bending bands at 2265 and 875 cm\(^{-1}\), respectively [8.6]. This rules out OH formation mechanisms based on molecular H\(_2\); if H\(_2\) broke an Si-O bond of a siloxane group, an SiOH and an SiH group would be expected to form. Therefore, reaction (8.5) could involve H\(_2\)O as well.

### 8.4.2 SiO(s) Band Interpretation

The reason that the films discussed in the paper are particularly susceptible to post-deposition OH incorporation is that the material has a significant number of highly distorted Si-O-Si bonds which are more reactive than relaxed Si-O-Si bonds. For example, as shown in Fig. 8.5, the SiO(s) spectral peak of the first spectrum is at 1056 cm\(^{-1}\), whereas the peak position of the band in thermally-grown and relaxed oxides is at 1078 cm\(^{-1}\) [8.7]. The position of the spectral peak can be correlated with the average bond-angle at the oxygen atoms sites (i.e., the Si-O-Si angle) [8.8,8.9]. This angle is approximately 144° in relaxed thermal oxides, and is generally about 5-10° less in remote PECVD oxides. It is well
established that the reactivity of Si-O-Si groups is greater the smaller the bond angle at the oxygen site [8.10]. In addition, remote PECVD oxide films are less dense than fully relaxed thermal oxides. This is exemplified by higher etch rates in buffered HF, and by direct measurements of film thickness as a function of post-deposition thermal annealing [8.11]. This means that as-deposited films contain more reactive bonds and have a porosity that allows for rapid diffusion of small molecules.

The changes that take place in the spectral peak and width of the SiO(s) band with increasing OH incorporation substantiate this picture. Specifically, with increasing OH incorporation, the spectral peak shifts to higher wavenumber and the FWHM decreases. Both of these trends are in accord with a removal of Si-O-Si bonds on the low wavenumber side of the distribution. This is further exemplified in a steepening of the low wavenumber side of the SiO(s) band. As these narrower angle bonds are removed, the distribution of absorbing SiO units in the film shifts to wider angle bonds, and the overall spread in the distribution diminishes (FWHM decreases). Moreover, the remote PECVD SiO₂ films can be made immune to attack by atmospheric water by annealing for short-times at sufficiently high temperatures, >700-800°C (Fig. 8.9.) Heating the oxide reverses the OH formation reaction, and provides enough molecular motion for most of the bonds to rearrange to a more relaxed state [8.12]. The temperature, time product of the furnace anneal (FA) used in these experiments was insufficient to completely relax the remote PECVD oxide. However, it has been shown elsewhere that FA or rapid thermal annealing (RTA) at higher temperatures, >1050°C for 100s, can render remote PECVD oxides indistinguishable from thermally grown oxide processes at the same temperature [8.12].

As the Si-O-Si bond angle decreases, the Si-O-Si group becomes more reactive, and the attack of these groups by water converts them to near-neighbor Si-OH groups. If it is assumed that the spectral width of the Si-O band derives from a distribution of Si-O-Si bond angles, then the low wavenumber side of this band (wavenumbers below the spectral
peak) is associated with the most reactive bonds. This is consistent with the shift of the SiO(s) spectral peak to higher wavenumbers in the films which have been exposed to water vapor and then display the symmetric OH(s) feature. The decrease in the FWHM of the SiO(s) feature is a subtractive effect and results from the removal of the low wavenumber side of the band.

8.4.3 OH(s) Band Interpretation

By examining the initial asymmetric OH band and knowing the local environments of silanol groups and the interactions between silanol groups about the distribution of silanol groups in the film can be determined. The vibrational modes of silanol groups are affected by hydrogen-bonding interactions. Based on previously reported studies of SiOH and OH bands in a variety of organic materials, the structure of the OH(s) band derives from hydrogen bonding interactions between the positive space charge of the H atom of the OH group and the negative space charge regions of the host material [8.13]. In addition it has been observed that as the OH···O distance decreases, the H-bonding strength increases and the frequency of the O-H stretching vibration decreases [8.14]. The character of the vibrational modes of Si-OH groups is strongly affected by hydrogen-bonding interactions [8.14,8.7]. In many organic materials the position of the OH(s) band shifts to lower wavenumbers with increasing hydrogen-bonding interactions [8.15].

It is known that as the O···O distance decreases, the H-bonding strength increases and the frequency of the O-H stretching vibration decreases [8.16]. These interactions occur between the H-atom of the OH group and O-atoms of the host network, as in the case of SiO₂, or O-atoms of other OH groups in alcohols and related compounds [8.14, 8.15]. It has been shown that the oscillator strength for the high wavenumber absorbing configurations is about five times weaker than for the low wavenumber configurations [8.17-8.29]. The negative space charge regions are associated with the non-bonding electrons of oxygen atoms in both siloxane (Si-O-Si) and silanol (SiOH) groups. Because
between oxygen atoms of these groups, e.g., 0.02-0.08 Å, can easily produce shifts in the ir active OH(s) frequency as large as 50-200 cm⁻¹ [8.14-8.16].

There are three possible local environments in which the Si-OH groups in an SiO₂ can exist: 1) as near-neighbor Si-OH groups; 2) as Si-OH groups that are partially shielded from other Si-OH groups; and 3) as Si-OH groups that are effectively isolated from other Si-OH groups by the Si-O-Si network. That the symmetric feature at 3350 cm⁻¹ and the asymmetric feature at 3650 cm⁻¹ are associated with the extreme cases as denoted above by 1) and 3), respectively. The local environment that provides the strongest H-bonding interaction is between neighboring Si-OH groups. At the other extreme, where the Si-OH group is effectively isolated from other Si-OH groups by the Si-O-Si network, there is only a weak interaction between the H-atom of the Si-OH group and the O-atoms of the Si-O-Si network. This weak interaction establishes the high wavenumber cut-off for the band, at 3650 cm⁻¹ for OH groups that are virtually free of any significant H-bonding interactions; e.g., OH groups on the surface [8.14]. This means that the vibrational frequencies at the high wavenumber side of the asymmetric band are primarily related to SiO₂ network H-bonding interactions with isolated Si-OH groups. The other Si-OH groups shift to lower wavenumber due to H-bonding interactions with other partially shielded Si-OH groups. These interacting Si-OH groups are not necessarily related to nearest neighbor Si-atoms in the network structure.

Observations of the growth rate of the OH peak show that Si-OH groups exist in two distinct environments: 1) as randomly-spaced OH groups that are incorporated via a relatively fast reaction during deposition or sample cool-down; and 2) as near-neighbors pairs of Si-OH groups that are hydrogen-bonded to each other and are introduced by exposure to atmospheric water vapor [8.4,8.5]. The isolated groups are associated with post-deposition reactions that occur during cool-down in the chamber, rather than with the heterogeneous deposition reactions. The rate of reaction is presumed to depend on the
not absorb additional water later on. Significant structural relaxation is evidenced by a shift of the SiO(s) band peak towards 1078 cm\(^{-1}\), the thermal oxide position after the FA. The average Si-O-Si bond angle must therefore shifts to higher values, which is permitted by the movement of atoms during the annealing process. Of course, by growing the films at a high enough temperature, 400°C, it is possible to create films that are not susceptible to OH incorporation, even without further processing.

8.5 Summary

There are two ways in which silanol groups can form in oxide films deposited at low temperatures by remote PECVD. Both of these are extrinsic processes, and the active species in these processes are: 1) OH species present in the chamber as a by-product of the deposition reactions, evidenced by an asymmetrically shaped OH(s) band at 3650 cm\(^{-1}\); and 2) H\(_2\)O present outside the chamber in the atmosphere which produces a symmetrically shaped OH(s) band centered about 3350 cm\(^{-1}\). Atmospheric H\(_2\)O preferentially reacts with Si-O-Si groups with smaller bond angles [8.10]. These bonds are more reactive than relaxed Si-O-Si bonds, and are more accessible to attack because of localized increases in the bond-free volume that are evident in the increased etch rates of these films in buffered HF [8.11,8.20]. The molecular species and the reaction pathway for intra-chamber OH incorporation appears to be different than the atmospheric mechanism. At this time it is not possible to propose a specific OH containing species or a particular pathway that will lead to random, rather than spatially correlated, silanol groups.

We have further shown that a-Si:H films (with about 5 at. % H and 800Å thick) can act as diffusion barriers that serve to prevent OH incorporation in the chamber and in the laboratory ambient. Flash annealing the films immediately after deposition not only relaxes the bond-angle distribution [8.12], but also renders the film immune to attack by atmospheric water with two mechanisms contributing to the chemical inertness: 1) the relaxation of the Si-O-Si bond angle distribution to larger bond angles, and hence less


9 Process Behavior

This chapter presents theoretical work to explain how excitation frequency and geometry affect power coupling, and how the reactor geometry affects diffusion of downstream injected gases and reaction rates. The first section discusses how the plasmas are affected by the excitation frequency, and describes the impact on coupling to charge extraction. The second section discusses how the downstream injected gases diffuse within the reactor to demonstrate the significance of backdiffusion. The final section discusses issues involved with chamber size affects the relative magnitudes of heterogeneous and homogeneous reaction rates.

9.1 Plasma Generation

This section discusses the effect of excitation frequency on the coupling mode with the plasma. The use of different excitation frequencies permits tailoring the electron energy distribution function (EEDF), to alter the dominant excitation states of molecular and ionic species [9.1]. The behavior of the copper coil under the influence of a 13.56 MHz and a 2.54 GHz signal is considered.

Power is delivered to the plasma through a coaxial cable from a matching network and an rf applicator consisting of a ten turn copper coil. The electromagnetic wave propagates through the cable in the TEM mode (transverse electric and magnetic field; both \( \mathbf{E} \) and \( \mathbf{B} \) field vectors are perpendicular to the conductor.) If no applied external field interferes with transmission, it is assumed that the TEM mode continues after the wave leaves the coaxial jacket. There are two directions in which the field may couple with the plasma, 1) in which the plasma acts like a core of a solenoid (Fig. 9.1a), \( \mathbf{E} \) is the potential drop across the coil due to self-induction, and 2) in which the coil is one electrode and the plasma is the other electrode of a capacitor (Fig. 9.1b), so that \( \mathbf{E} \) is radial with respect to the coil. In the first mode, the \( \mathbf{B} \) field causes the electrons in the plasma tube circulate to create an opposing current, with energy being imparted along the length of the tube, the
-186-
coils have a net inductive impedance. In the second mode, the coil may be considered a hollow cylinder, it is known as a capacitive coupling mode.

![Diagram of E and B vectors](image)

**Figure 9.1- Diagram of E and B vectors for a) inductance and b) capacitance between the rf coil and the plasma.**

It is possible to show how the fields vector are oriented with respect to the plasma by determining whether the fields allow for a net capacitive or inductive impedance. A rough estimate of the ac impedance components of the system may be made by the following argument. When determining the ac impedance components of the impedance function, the phase vector points in the direction of the larger term. Therefore, the ac impedance term with the larger magnitude determines the character of the impedance. Impedance is defined as follows, with the L term accounting for induction, and the C accounting for capacitance,

\[
Z^2 = R^2 + \left[ 2\pi fL - \frac{1}{2\pi fC} \right]^2
\]

(9.1)

\[
L = \mu_0 h^2 l A, \quad C = \frac{\kappa \varepsilon_0 l}{\ln(b/a)}
\]

where, \( f \) is the applied frequency, \( l \) is the coil length, \( A \) is the cross-sectional area, \( h \) is the loop density, \( b \) is the coil radius, \( a \) is the plasma radius, \( \kappa \) is the dielectric coefficient, \( \mu_0 \) is the permittivity, and \( \varepsilon_0 \) is the dielectric constant. The dimensions of the rf coil geometry
are, 5.1 cm diameter, 10 turn, and 10 cm long, and f at 13.56 MHz. Assuming that the gap between the plasma and the coil is filled with fused silica dielectric, \( \kappa \) is 3.8. The calculation yields a 215\( \Omega \) inductive impedance, and a 985\( \Omega \) capacitive impedance. Since the impedance is dominated by the capacitive component, the plasma coupling under these conditions shows a net capacitive coupling. The cross-over point, (i.e. resonance frequency), between net capacitive and inductive coupling is given by

\[
f_r = \frac{1}{2\pi} \sqrt{\frac{1}{LC}} \tag{9.2}
\]

which is 29.0 MHz. At the resonance frequency, matching is perfect with the plasma, i.e., there will be no reflected power, and energy is coupled into the plasma like a resistor. The fact that the cross-over occurs within a factor of two from the rf frequency implies that small changes in the frequency or geometry of the applicator produces appreciable changes in the coupling mode. In addition, if the same applicator was used at the 2.54 GHz frequency, the coupling would be inductive. Finally, because the 13.56 MHz discharge couples capacitively, the rf coil is seen by the plasma to be a conductive hollow cylinder rather than a coil.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>( Z_L )</th>
<th>( Z_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.56 MHz</td>
<td>( 2.15 \times 10^2 \Omega )</td>
<td>( 9.85 \times 10^2 \Omega )</td>
</tr>
<tr>
<td>2.54 GHz</td>
<td>( 4.02 \times 10^4 \Omega )</td>
<td>( 5.26 \times 10^0 \Omega )</td>
</tr>
</tbody>
</table>

The microwave applicator couples power into the plasma by inductive coupling. The waveguide is grounded to the chamber potential through the support frame, and ground electrode of the coaxial cable. It is different than the rf antenna because the antenna is an extension of the biased conductor of the coaxial cable. Even though the geometry between the rf and microwave applicators is different, the proximity of resonance
frequency to 13.56 MHz rather than 2.54 GHz is an indication that the coil of the rf applicator couples inductively at 2.54 GHz.

9.2 Gas Mixing

The deposition reactions in the remote PECVD system are initiated when excited species formed in the plasma tube mix with the compounds injected into the chamber through the gas dispersal rings. The degree to which downstream injected gases backdiffuse towards the plasma governs the reactions that dominate. In addition, when the traversal time from plasma tube to substrate is similar to the characteristic decay time of plasma generated species, then the plug velocity is an important parameter.

With a simple one-dimensional gas diffusion model, it is possible to approximate the concentration of injected gaseous species along the length of the chamber. The model assumes 1) steady-state flow, 2) no significant pressure gradient in the reactor, and 3) no significant flow disruptions produced by the plasma tube/chamber joint, or by subsidiary ports for sampling or pumping. Figure 9.2 shows a schematic diagram of the model, where one component is injected at one end of the smaller tube, and the second component is injected into the larger tube. The flux differential volume for a tube with gas flowing through it is defined,

\[ n A \frac{dx}{dt} \frac{dc}{dx} = J_1 - J_2 + J_3 - J_4 \]  \hspace{1cm} (9.3)

where, \( x \) is the distance from the differential volume boundary, \( J_1 \) and \( J_2 \) are the drift flux components into and out of the volume, and \( J_3 \) and \( J_4 \) are the diffusion components into and out of the volume, \( v \) is the plug velocity of the tube, \( A \) is the cross-sectional area, \( n \) is the molar density of particles, \( D \) is the diffusion coefficient of, \( c \) is the concentration. Through combination of the flux terms equation (9.3) becomes,
\[
\frac{dc}{dt} = v \frac{dc}{dx} + D \frac{d^2c}{dx^2}. \quad \text{at steady-state} \quad \frac{d^2c}{dx^2} + \frac{v}{D} \frac{dc}{dx} = 0. \quad (9.4)
\]

Figure 9.2- a) Schematic diagram of back diffusion flux components, and b) Schematic diagram of the backdiffusion profile for segments within the chamber.

Solving this second order homogeneous differential equation yields,

\[
c = c_0 \exp\left(-\frac{v}{D} x\right). \quad (9.5)
\]

The solution is for a single cylinder in which the downstream gas is injected along its axis. For the remote PECVD chamber, two joined tubes of different diameters must be considered. The variable \(x\) is the distance from the downstream tube injection point, and \(I\) is the distance between the end of the plasma tube, (position \(x_1\)), and the gas dispersal ring, (Fig. 9.2b). There are three regions defined by this system based on their position relative to the two gas injection points; 1) \(x \geq 0\), positions downstream from the gas dispersal ring, 2) \(x_1 \leq x < 0\), positions downstream from the plasma tube end, and upstream from the gas
\[ D_{12} = 2.446 \times 10^4 T^{3/2} \left[ \sqrt{\frac{(M_1 + M_2)}{M_1M_2}} \frac{1}{P \sigma_{12}^2 \Omega_D} \right] \] (9.10)

where, \( D_{12} \) is expressed in cm\(^2\)/s, \( P \) is in mTorr, \( T \) is in K, \( M \) are in amu. \( \Omega_D \) and \( \sigma_{12} \) are estimated from the Lennard-Jones potential. The tables from which these values are derived are listed in Appendix 11.3 [9.2]. For gas pairs used in this work, the calculated diffusion coefficients are listed in Table 9.2:

<table>
<thead>
<tr>
<th>Gas</th>
<th>( D_{12} ) (cm(^2)/s)</th>
<th>Gas</th>
<th>( D_{12} ) (cm(^2)/s)</th>
<th>Gas</th>
<th>( D_{12} ) (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/H(_2)</td>
<td>4.033 \times 10^3</td>
<td>He/NH(_3)</td>
<td>2.068 \times 10^3</td>
<td>H(_2)/SiH(_4)</td>
<td>1.528 \times 10^3</td>
</tr>
<tr>
<td>He/SiH(_4)</td>
<td>1.471 \times 10^3</td>
<td>He/N(_2)O</td>
<td>1.552 \times 10^3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He/SiH(_2)Cl(_2)</td>
<td>1.1 \times 10^3</td>
<td>He/HCl</td>
<td>1.765 \times 10^3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He/O(_2)</td>
<td>1.900 \times 10^3</td>
<td>He/N(_2)</td>
<td>1.777 \times 10^3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.3 shows backdiffusion profile for 10 sccm 10% SiH\(_4\) + He injected downstream for different chamber diameters and He flow rates. It shows that the 15 cm diameter chamber with 200 sccm He has 55% SiH\(_4\) concentration at the mouth of the plasma tube compared with the injection point. Decreasing the tube diameter to 5 cm, lowers the concentration to negligible values (<1%), while decreasing the He flow to 100 sccm increases the backdiffusion substantially to about 20%. All modes have negligible concentrations (<1%) at the edge of the power applicator. The 55% concentration of backdiffusing gas at the mouth of the plasma tube explains why the deposition rate is so high upstream of the gas injection point in the 15 cm diameter chamber.
Figure 9.4 shows the backdiffusion for a variety of gases flowing at 10 sccm, with 200 sccm He injected into the plasma tube. It shows that for gases injected into the remote plasma reactor, the concentrations at the plasma tube mouth vary by more than 30%, with H₂ backdiffusing the most effectively, and SiH₂Cl₂ backdiffusing the least effectively. All of the gases had a negligible concentration at the edge of the power applicator.

9.3 Surface Area

As shown in section 9.2, the chamber diameter/plasma tube diameter ratio affects the degree of backdiffusion because of the plug velocity ratios of the two tubes. However, the reactor volume/surface area can affect the surface reactions too. The volume/surface area ratio affects the ratio of surface to gas phase reaction rates by altering the ratio of reaction sites for heterogeneous and homogeneous reactions. Narrower diameter chambers transport active species to walls more efficiently. For example, gas phase polymerization may be limited by decreasing the transit time of SiH₂ to a wall site. This may be accomplished by increasing the average thermal velocity, or by decreasing the average distance from generation site to the wall. The 5.1 cm diameter chamber used for the oxide growth study promotes the H₂O reaction with the oxide over the 15.3 cm diameter reactor, because the lower total surface area of the chamber increases the substrate/chamber area ratio. For cylindrical chambers, the volume/area ratio is:

\[
R = \frac{V}{A} = \frac{1}{2} \frac{rz}{r + z}
\]  

(9.11)

where, \( r \) is the chamber radius, and \( z \) is its length. For a 43 cm chamber, with the diameters listed above, the narrower chamber ratio is 1.18 cm, and for the wider chamber ratio is 3.23 cm. This means that the wider chamber has proportionally 2.75 times more volume than the narrower chamber. If a species can participate equally fast in surface or gas phase reactions, then the wider chamber has a homogeneous/heterogeneous consumption rate of the species that is 3 times greater than the narrow chamber. The fraction of surface area is greater for the narrower chamber too. This means that a given surface receives a
greater fraction of reaction products by the ratio of the reactor surface areas. If the reactions
are not surface-limited, then they proceed 9.2 times faster on a unit surface area in the
narrow reactor. If the flow rates, pressure, and power level are the same for the two
reactors, then the higher ratio implies that a greater fraction of H₂O adsorbs on the substrate
placed in the narrow reactor.

References


10 Summary

The thesis described the 5 cm and 15 cm diameter reactors used for this thesis in Chapter 2. In addition, it described the two different power supplies and applicators used for generating 13.56 MHz and 2.54 GHz discharges. The design and operation of the quadrupole mass spectrometer were also explained. In addition, design, construction, and theory of a single and double Langmuir probe were described.

The effects of excitation frequency, power, and nitrogen source gas concentration from the substrate on $T_e$ and $n_e$ were discussed in Chapter 3. It has been shown that excitation frequency affected the coupling mode between the power supply and the plasma. At 13.56 MHz, the coupling was capacitive. This coupling mode utilized both the power applicator and the chamber as electrodes. The ramification was that the $E$ fields penetrate into the chamber which increased the charge concentration in the chamber, and provided for electron acceleration near grounded chamber fixtures. At 2.54 GHz the coupling mode was inductive. Inductive coupling had a net $E$ field along the tube radius, thus minimizing $E$ field leakage into the chamber. Therefore, inductively coupled plasmas only diffused towards the chamber due to bulk gas flow and thermal diffusion of particles. The bulk of electron impact processes was confined to the applicator region of the plasma tube.

Several aspects of the a-Si:H reaction chemistry for remote PECVD were discussed in Chapter 4. An additional silane ionization source in the afterglow was identified, it was probably $\text{He}^*$, but it did not significantly contribute to deposition. Polysilane species were formed in the afterglow, and were likely to be a significant factor in film growth. Finally, the exact deposition Si-containing precursors could not be conclusively determined using the current geometry of the mass spectrometer enclosure.

Microcrystalline silicon deposition was the subject of Chapter 5. It was shown that $\mu\text{c-Si}$ could be deposited under identical conditions noted for other reactors. Under these conditions, mass spectrometry showed that the concentration of disilane and polysilanes
dropped by a factor of 4-5. It was assumed that the drop in disilane production was caused by a decrease in SiH₂ concentration and an increase in SiH₃. It was reasonable according to SiHₓ, H, H₂ reaction rate tables for an increase of the H/Si ratio in the reactor. It was considered that the presence of reactive polysilane species promoted a-Si:H film growth over μc-Si growth.

Low temperature selective silicon epitaxy was discussed in Chapter 6. This chapter showed that it was possible to selectively deposit epitaxial silicon at temperatures below 300°C, but the process required a preloading step. The breakup pattern of SiH₂Cl₂ in the plasma was shown by mass spectrometry. By substituting D₂ for H₂, it was shown that mixing of H and D occurs with SiH₂Cl₂, but the mixing was not complete. When hydrogen was added to the discharge and SiH₂Cl₂ was present downstream, H₂Cl⁺ formed. A superacid ion mechanism was postulated as a candidate for controlling the selective silicon deposition process, by permitting preferential removal of silicon from non-silicon surfaces.

Chapter 7 presented results of depositions of silicon nitrides with NH₃ and N₂ source gases and microwave and rf discharges. Deposition of nitride films from N₂/He gas mixtures was achieved with rf excitation, but not with microwave excitation. The differences in bonded hydrogen for substrate placement were consistent with SiH₄ fragmentation and a silicon nitride reaction. Nitride films were obtained for both rf and microwave excitation of NH₃/He mixtures, but the deposition reactions were driven primarily by atomic H and electron excitation of SiH₄. Microwave excitation of NH₃/He showed that at low concentrations of NH₃ yields films are dominated by Si-NH bonding, while higher concentrations of NH₃ displayed significant concentrations of SiH groups. The study also showed that NH incorporation helped relax the network as shown by increasing SiN(s) wavenumbers with increasing [NH].
The effects of reaction by-products and post deposition treatments on silicon oxide films were discussed in Chapter 8. It was shown that OH groups in the oxide do not accumulate in the film until the film is cooled after deposition, or until the sample is exposed to ambient air. However, placing a diffusion barrier over the film before cooling it prevented OH formation. Also, a post deposition anneal relaxed the film so OH uptake did not occur. The OH was incorporated by H₂O that diffused into the film and reacted with narrow-angled Si-O-Si groups. The sources of H₂O were wall sites that adsorb H₂O which was a deposition reaction by-product or from moisture in the air. In addition the 925 cm⁻¹ vibrational mode was shown to be a the result of a hybridized vibration between neighboring hydrogen-bonded OH groups.

Chapter 9 examined some of the issues associated with various parts of the process. It examined coupling of power into the plasma, and how frequency leads to different coupling modes. It looked at backdiffusion of gases injected at the gas dispersal ring, and showed how chamber diameter affects plug velocity and backdiffusion. The last section, dealt with the effects of chamber size on homogeneous and heterogeneous reaction rates.

This thesis presented a study of the segments of the remote plasma process. Remote plasma has the potential for low thermal budget processing of semiconducting materials with minimal damage to substrates. The technique makes use of non-constant gas flow and chamber geometry to control the direct plasma excitation of certain species. Depending on the excitation frequency, the geometry of the power applicator permits capacitive or inductive coupling which governs the electron concentration in the reactor, hence controlling the a-Si:H deposition process. Work needs to be done in modeling the gas flow of the process, and in understanding how to control active species extraction into the chamber through the use of grids to control charged species, and collision engineering to control metastables and other non-charged excited species.
11 Appendices

The first section lists the code for the mass spectrometer operating program written in ASYST. The second section discusses an experiment that determines the sticking coefficient of radical using the mass spectrometer. It also derives an equation detailing the fraction of radicals lost to the sniffer tube based upon the loss probability. The third section provides data tables for the calculation of diffusion coefficients. The fourth section describes the equation for estimating the electron decay equation based for charged particles injected into a moving gas flow.

11.1 Mass Spectrometer Control Program

The program listed below is used to control the Extrel C-50 mass spectrometer using an PC 386 computer and a DT2800 data translation board. The program is written in ASYST 3.0. The memory requirement is 3 Mbytes expanded memory, and DOS 4.0.

\ Developed by Jeremy A. Theil 9/1/91.
\ The primary attribute of this program, is that it can READ \ & WRITE 3 different
\ MASS data files, including the old fixed data point (100), fixed resolution
\ (0.1 amu), & a variable resolution and mass range format. The program can also
\ handle 2 different ENERGY scan file types, the old fixed data point (1000 pts
\ and 0.1 eV res), and a new variable length and resolution file. Scan
\ parameter entry has been simplified by creation of an editing window. The
\ program can handle up to 20 registers, and perform batch functions on
\ consecutively numbered files. The maximum number of points in the spectra is
\ limited to the value of the scalar ARRAY.PTS. Original data acquisition
\ routine concepts by D. V. Tsu.

\ STAT [ 1 ] TYPE  0  1  2  3  4
\ STAT [ 2 ]  LM  LEE  LM  LEE
\ STAT [ 3 ]  HM  HEE  PTS#  HM  HEE
\ STAT [ 4 ]  EE  EMAS  EE  EE  EMAS
\ STAT [ 5 ]  SEN  SEN  SEN  SEN  SEN
\ STAT [ 6 ]  GN  GN  GN  GN  GN
\ STAT [ 7 ]  RE  RE  RE  RE  RE
\ STAT [ 8 ]  -  -  -  RESOL  RESOL
\ STAT [ 9 ]
\ STAT [10 ]

\ NOTE: This program must be run with an EXPANDED memory manager. If one is not
\ available, version 46 or earlier must be used. Version 46 can only handle 6
\ registers, and does not contain the automated file handling features.

\ NOTE: If the peak position check is turned on, and the program cannot
\ determine the peak position accurately, it will print an error message,
\ return a value of -10.0 for the intensity, then move on to the next point.
CLEAR.FUNCTION.KEYS
32 STRING RETURN.TOK
TOKEN LM-TOK
TOKEN HM-TOK
TOKEN SC-TOK
TOKEN SCMIN-TOK
TOKEN Y-TOK
TOKEN INTENSITY \ Temporary array for scanning
TOKEN ENTRY* TOKEN X-ARRAY
TOKEN R1 TOKEN R2 TOKEN R3 TOKEN R4 TOKEN R5 TOKEN R6 TOKEN R7 TOKEN R8
TOKEN R9 TOKEN R10 TOKEN R11 TOKEN R12 TOKEN R13 TOKEN R14 TOKEN R15 TOKEN R16
TOKEN R17 TOKEN R18 TOKEN R19 TOKEN R20
TOKEN REAL.MASS
TOKEN PEAK.DATA

REAL SCALAR SC \ Scale for vertical axis
  SCALAR SCMIN \ Min. value for vertical axis
  SCALAR MMAX \ Mass max = 100, 200 or 400 AMU
  SCALAR SLP \ Slope correction factor
  SCALAR OFFSET \ Mass offset correction factor
  SCALAR EOFFSET \ Energy offset correction factor
  SCALAR ELM \ Expanded low mass
  SCALAR EXHM \ Expanded high mass
  SCALAR EEXCMIN \ Expanded low intensity
  SCALAR EXSC \ Expanded high intensity
  SCALAR A.BASE \ Amplitude of base
  SCALAR RESOL \ Data mass resolution
  SCALAR SLOPE
  SCALAR INTCP
  SCALAR STEP
  SCALAR HIGH
  SCALAR LOW

INTEGER SCALAR GN1 \ Gain code
  SCALAR VAL
  SCALAR RESCAN \ No. of times to repeat scans
  SCALAR VOUT \ Selects Vout to be 2.5V max. or 5.0V or 10.0V
  SCALAR ILOW \ Index for EXLM
  SCALAR IHI \ " " EXHM
  SCALAR PEN.COL
  SCALAR I.BASE1 \ Index of Baseline mass
  SCALAR I.BASE2
  SCALAR N.PEAKS \ Number of peaks to be monitored
  SCALAR ITER \ Counter for DATA.ARRAY.PRINT
  SCALAR MAXCOL \ # of columns on the page
  SCALAR MINCOL \ First column of peach page
  SCALAR COUNTER \ # of spectra in the file
  SCALAR COUNTER1 \ # of files counter
  SCALAR COUNTER2
  SCALAR COU
  SCALAR COU1
  SCALAR ARRAY.PTS \ # of points in the array
  SCALAR NUM.VAL
  SCALAR YPOS \ Row of cursor in menu
  SCALAR XPOS \ Column of cursor in menu
  SCALAR EXPAN.DVALUE \ Toggle value for display limits
  SCALAR MAX.VALUE \ Toggle display for maxima checker
  SCALAR AXIS.VALUE \ Toggle for axis display
  SCALAR SENS1 \ Value of sensitivity
  SCALAR HI
  SCALAR LO
  SCALAR START
  SCALAR FINISH
2000 ARRAY.PTS := \ Sets maximum data array length.
INTEGER SCALAR FIRST.LETTER 1 FIRST.LETTER :=
       SCALAR LAST.LETTER 20 LAST.LETTER :=

REAL DIM[ 12 ] ARRAY FILE.STATS
DIM[ 2100 ] ARRAY AXIS.BUFFER

DIM[ 100 ] ARRAY PEAK.MASS \ Selected peak masses
DIM[ 100 , 60 ] STRING.ARRAY SPECTRA.COMMENTS
DIM[ 100 , 8 ] STRING.ARRAY SPECTRA.NAMES

INTEGER DIM[ 10 ] ARRAY R1.STAT
DIM[ 10 ] ARRAY R20.STAT

8 STRING R1.NAME \ File names of the registers
8 STRING R2.NAME 8 STRING R3.NAME 8 STRING R4.NAME 8 STRING R5.NAME
8 STRING R6.NAME 8 STRING R7.NAME 8 STRING R8.NAME 8 STRING R9.NAME
8 STRING R10.NAME 8 STRING R11.NAME 8 STRING R12.NAME 8 STRING R13.NAME
8 STRING R14.NAME 8 STRING R15.NAME 8 STRING R16.NAME 8 STRING R17.NAME
8 STRING R18.NAME 8 STRING R19.NAME 8 STRING R20.NAME

64 STRING R1.COMMENT \ Comments for the registers
64 STRING R2.COMMENT 64 STRING R3.COMMENT 64 STRING R4.COMMENT
64 STRING R5.COMMENT 64 STRING R6.COMMENT 64 STRING R7.COMMENT
64 STRING R8.COMMENT 64 STRING R9.COMMENT 64 STRING R10.COMMENT
64 STRING R11.COMMENT 64 STRING R12.COMMENT 64 STRING R13.COMMENT
64 STRING R14.COMMENT 64 STRING R15.COMMENT 64 STRING R16.COMMENT
64 STRING R17.COMMENT 64 STRING R18.COMMENT 64 STRING R19.COMMENT
64 STRING R20.COMMENT

1 STRING EXIT.SAVE \ Routine exiting value.
4 STRING SENSITIVE \ Sensitivity factor of mass spectrometer
30 STRING XEQ.FUNCTION \ MASS or ENERGY command string
17 STRING FORE.COLOR \ Window foreground color
17 STRING BACK.COLOR \ Window background color
8 STRING TERM \ Window functions' prefix
16 STRING VAL$ \ String equivalent of current value
16 STRING DIRECTORY.IN \ Name of current Directory
16 STRING DIRECTORY.OUT \ Name of current Directory
8 STRING ROOT.NAME \ Root string of filenames
1 STRING YN? \ YES or NO register
3 STRING REG \ Register containing R1 thru R20
14 STRING NAME \ Current filename
64 STRING AUTO.COMMAND \ Command string for AUTO.OPEN routine

\ Window definitions
5 5 20 74 WINDOW (OTHER)
25 3 28 79 WINDOW (WORKSPACE)
29 0 29 79 WINDOW (BOTTOM)
27 0 27 0 WINDOW (AXIS)
28 0 28 1 WINDOW (REGISTER)
29 36 29 38 WINDOW (VIEW)
3 5 20 44 WINDOW (PARAMETER)
9600 SET.BAUD

\ I/O Definitions
DT2800 \ Set current DAS device to DT2800
1 1 D/A.TEMPLATE MASS.DA \ Mass output
0 0 D/A.TEMPLATE ENERGY.DA \ Electron energy, Chnl 0
0 0 A/D.TEMPLATE INT \ Intensity at mass MASS.DA
4 DIGITAL.TEMPLATE SENS \ Controls the sensitivity, write to Port 0
5 DIGITAL.TEMPLATE RANGE \ Controls the output range, write to port 1

MASS.DA D/A.INIT
ENERGY.DA D/A.INIT
INT A/D.INIT
DIGITAL.INIT

: CAT+ "CAT "EXEC ;

: TERM? TERM " MASS" "- ;

: "TERM TERM "SWAP CAT+ ;

: STAT REG " .STAT" CAT+ ; \ Catenates REG.STAT

: "CMPSS 32 "COMPRESS ;

: TAB 9 ASCII" "TYPE ;

: TV 0 .14 1.1 STORE.VIDEO(AUTO) ;

: LEN \ Length of status array header.
  STAT [ 1 ] 3 < IF
    7 ELSE 10 THEN
  ;

: INITIAL.VALUES
  " RI" REG ":= 1 REG#: 0.5 SC :=
  1 GNR := 0.1 RESOL := 1 ILOW := 0. SCMIN := 5 RESCAN :=
  " High" SENSITIVE ":= 3 SENSI := " MASS" TERM ":= " A:" DIRECTORY,IN ":=
  " A:" DIRECTORY.OUT ":="
  32 VOUT := \ Default Vout = 2.5V max
  1. NMAX := 12 PEN.COL := 1 MAX.VALUE :=
  1.0318 SLP := 0.0 EOFFSET := 0 EXPAND.VALUE :=
  -1.939 OFFSET := "NULL VALS ":= 10 I.BASE1 := 10 I.BASE2 :=
  ;

: MASS.INITIAL.VALUES
  0 STAT [ 4 ] = IF

: ENERGY.INITIAL.VALUES
  0 STAT [ 4 ] = IF

: RECOUP \ Resets the display to normal screen
  DEVICE.INIT DEF.VPORT
  IBM.GRAPHICS DEVICE.INIT
  ;
: MAX.CHECK \ Checks the extrema values of the spectrum
1 MAX.VALUE = IF
REG "EXEC SUB[ ILOW , IHI ILOW - 1 + ] []MAX SC-TOK >= IF
REG "EXEC SUB[ ILOW , IHI ILOW - 1 + ] []MAX SC SCMIN - 0.1 * + EQUIV> SC-TOK
." "Resetting Intensity Maximum!"
THEN
REG "EXEC SUB[ ILOW , IHI ILOW - 1 + ] []MIN SCMIN-TOK <= IF
REG "EXEC SUB[ ILOW , IHI ILOW - 1 + ] []MIN EQUIV> SCMIN-TOK ." "Resetting Minimum!"
THEN
THEN
;
: Y.OR.N \ Yes or No answer function
BEGIN
PCKEY
CASE
78 OF ." N" " N" YN? " := TRUE ENDOF
110 OF ." N" " N" YN? " := TRUE ENDOF
89 OF ." Y" " Y" YN? " := TRUE ENDOF
121 OF ." Y" " Y" YN? " := TRUE ENDOF
FALSE
ENDCASE
UNTIL
;
: PROMPT \ Picks current array
." 1 thru 20? "
BEGIN
#INPUT
DUP DUP FIRST.LETTER >= LAST.LETTER <= AND IF
DUP REG# := " R" "." "CAT "CMPSS TRUE ELSE
DROP FALSE
THEN
UNTIL
REG ":= CR
{REGISTER} 3 0 FIX.FORMAT REG# .
8 4 FIX.FORMAT
PREVIOUS.WINDOW
;
: X-AXIS  \ This function creates the proper X-axis when needed
REAL ARRAY.PTS RAMP
2 STAT [ 1 ] = IF 0.1 THEN
* STAT [ 2 ] +
;

: FIND.INDEX.FXD.PT
;

: FIND.INDEX.FXD.IC
STAT [ 2 ] - RESOL 1.0 * /
;

: INDEX  \ Returns index of mass value, using previous two functions
STAT [ 1 ] CASE
0 OF FIND.INDEX.FXD.PT ENDOF
2 OF FIND.INDEX.FXD.IC ENDOF
3 OF FIND.INDEX.FXD.IC ENDOF
ENDCASE
;

: AVERAGE.Y  \ Averages the Y-value about the given mass
0 A.BASE :=
DUP 5 + SWAP 5 - DO
A.BASE REG "EXEC [ I ] + A.BASE :=
LOOP
A.BASE 10 /
;

: FLATTEN?
." Give the first mass point." #INPUT CR
INDEX I.BASE1 :=
." Give the second mass point." #INPUT CR
INDEX I.BASE2 :=
;

: FLATTEN  \ Removes linear background from spectrum
I.BASE1 PTS# > I.BASE2 PTS# > OR IF
." Cannot flatten properly. Please pick new points." CR
FLATTEN?
MYSELF THEN
I.BASE1 AVERAGE.Y I.BASE2 AVERAGE.Y -
SLOPE := \ Slope find
I.BASE1 AVERAGE.Y X-AXIS [ I.BASE1 ] SLOPE * - INTCP := \ Offset find
REG "EXEC X-AXIS SLOPE * INTCP + - REG "EXEC :=
;

: FLATTEN!
PROMPT
FLATTEN
;

: AXIS?
{AXIS}
AXIS.VALUE 1 = IF 0 AXIS.VALUE := ." N" ELSE
1 AXIS.VALUE := ." Y" THEN
PREVIOUS.WINDOW ;
: MAX?
   ." Maxima checker turned "
  MAX.VALUE 1 = IF 0 MAX.VALUE := ." OFF." ELSE
  1 MAX.VALUE := ." ON." THEN

; Converses the input
: CONVERT
   INT STAT [ 7 ] TEMPLATE.REPEAT \ Set the Repeat factor to RE
   A/D.IN
   INT A/D.IN                     \ Input, puts RE numbers on the stack
   1. *                          \ Converts Integer no. to Real no.
   STAT [ 7 ] 1 DO               \ This allows us to add up the nos.
   +                             \ to a no. greater than 32000,
   LOOP                           \ which is the limit of Integers.

; MASSES.DATA \ Sets the mass command of the C-50.
MASS.DA D/A.INIT
   SLP * OFFSET + \ Correction for gain and offset
   40.95 * MMAX / 4095 SWAP - D/A.OUT
;

: ENERGY.DATA \ Sets the ionization energy (eV) of the C-50.
ENERGY.DA D/A.INIT
   EEOFFSET +
   40.95 * 4095 SWAP - D/A.OUT
;

: SET.MASS.RANGE
   STAT [ 3 ] 100. <= IF 32 VOUT := 1. MMAX :=
   ELSE STAT [ 3 ] 200. <= IF 64 VOUT := 2. MMAX :=
   ELSE STAT [ 3 ] 400. <= IF 128 VOUT := 4. MMAX :=
   ELSE STAT [ 3 ] 400. > IF ." Too large mass !" " MENU.INIT" "EXEC THEN
   THEN THEN THEN
   RANGE DIGITAL.INIT
   VOUT DIGITAL.OUT
   CR
;

\ ------------------ Menu Window Routines ------------------
: SCAN.VALUE.WINDOW \ Initializes the window
   STACK.CLEAR
   TV
   STORE.function.KEYS
   CLEAR.function.KEYS
   NORMAL.DISPLAY
   BLACK MIX BACKGROUND SCREEN.CLEAR (BOTTOM)
   BLACK MIX BACKGROUND (PARAMETER)
   FORE.COLOR "EXEC MIX FOREGROUND
   BACK.COLOR "EXEC MIX BACKGROUND
   SCREEN.CLEAR (BORDER)
PRINT HEADINGS  \ Sets up the window display
TERM ".INITIAL.VALUES" CAT+
8 3 FIX FORMAT
TERM? IF
." MASS SCAN & VIEWING PARAMETERS" ELSE
." ENERGY SCAN PARAMETERS" THEN
CR ." # of Scans: " RESCAN .
CR ." Sig Intens Max: " SC .
CR ." Min: " SCMIN .
CR ." Sensitivity: " SENSITIVE "TYPE
CR ." Enrgy Offset(eV): " EOOFFSET .
;
DELETE CHAR  \ Function to erase characters
DROP XPOS 27 < IF "NULL VALS ":= 27 XPOS := 27 YPOS GOTO.XY ." THEN
XPOS 27 := IF
XPOS 1 - XPOS := XPOS YPOS GOTO.XY ." 
VALS "DUP "LEN DUP 1 = IF
"NULL VALS ":= ELSE
1 - "LEFT VALS ":= THEN THEN
;
EDIT ENTRY  \ Accepts and manipulates typed characters
BEGIN
PCKEY DUP DUP CASE
80 OF DROP TRUE ENDOF \ DOWN
72 OF DROP YPOS 2 - YPOS := 0 YPOS = IF NUM#VAL YPOS := THEN
TRUE ENDOF \ UP
73 OF DROP XPOS 1 + XPOS := FALSE ENDOF \ RIGHT
75 OF DROP DELETE CHAR FALSE ENDOF \ LEFT
27 OF DROP ESCAPE ENDOF
13 OF DROP TRUE ENDOF
8 OF DELETE CHAR FALSE ENDOF
ASCII" "DUP
XPOS YPOS GOTO.XY "TYPE
XPOS 1 + XPOS :=
VALS "SWAP "CAT VALS ":= FALSE
ENDCASE
UNTIL
XPOS 39 > IF 39 XPOS := THEN
XPOS 27 < IF 27 XPOS := THEN
YPOS NUM#VAL > IF NUM#VAL 1 + YPOS := THEN
YPOS 0 - IF 1 YPOS := THEN
;
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: INPUT.NUMBER \ Accepts numerical input.
   EQUIV ENTRY 27 YPOS GOTO.XY 9 SPACES
   13 VAL$ "COMPRESS
   VAL$ "NULL " = NOT IF
   VAL$ 0 "NUMBER DUP ENTRY* :=
   27 YPOS GOTO.XY 10 SPACES
   18 YPOS GOTO.XY 19 SPACES
   THEN
   1 16 GOTO.XY 37 SPACES "NULL VAL$ ":-
   :
   : GAIN \ Set the intensity gain of on-board output converter
   STAT [ 6 ] INPUT.NUMBER
   STAT [ 6 ] CASE
   1 OF 1 GN1 := ENDOF
   4 OF 2 GN1 := ENDOF
   8 OF 3 GN1 := ENDOF
   RETRY MESSAGE.CASE EDIT.ENTRY MYSELF
   ENDCASE
   INT GN1 A/D.GAIN
   A/D.INIT
   :
   : SENSITIVITY \ Controls the sensitivity of the multiplier
   SENSI INPUT.NUMBER
   SENSI CASE
   1 OF 64 STAT [ 5 ] := " Low" SENSITIVE ":= ENDOF
   RETRY MESSAGE.CASE EDIT.ENTRY MYSELF
   ENDCASE
   SENS DIGITAL.INIT
   STAT [ 5 ] DIGITAL.OUT
   :
   : ENERGY.FILE.TYPE
   STAT [ 1 ] INPUT.NUMBER
   STAT [ 1 ] DUP 1 = 4 = OR NOT IF
   RETRY MESSAGE.CASE EDIT.ENTRY MYSELF THEN
   ;
: MASS.FILE.TYPE
STAT 1 INPUT.NUMBER
STAT 1 DUP DUP 0 = 2 = 3 OR OR NOT IF
RETRY MESSAGE.CASE EDIT.ENTRY MYSELF THEN
;
;
: EDIT.CASE \ Manipulates the data as needed
STACK.CLEAR
YPOS 1 - CASE
 1 OF ".FILE.TYPE" "TERM 8 0 FIX.FORMAT
18 YPOS GOTO.XY 18 SPACES
18 YPOS GOTO.XY STAT 1 . 8 3 FIX.FORMAT ENDOF
2 OF STAT 4 INPUT.NUMBER STAT 4 STAT 1 1 =
STAT 1 4 = OR IF MASS.DATA ELSE ENERGY.DATA THEN ENDOF
3 OF STAT 2 INPUT.NUMBER ENDOF
4 OF STAT 3 INPUT.NUMBER ENDOF
5 OF STAT 1 2 IF RESOL INPUT.NUMBER RESOL 1000 * STAT 8 :=
TERM? IF SET.MASS.RANGE THEN THEN ENDOF
6 OF RESCAN INPUT.NUMBER ENDOF
7 OF SC INPUT.NUMBER ENDOF
8 OF SCM IN INPUT.NUMBER ENDOF
9 OF SENSITIVITY 8 0 FIX.FORMAT
22 YPOS GOTO.XY 12 SPACES
22 YPOS GOTO.XY SENSITIVE "TYPE 8 3 FIX.FORMAT ENDOF
10 OF OFFSET INPUT.NUMBER ENDOF
11 OF EOFFSET INPUT.NUMBER STAT 4 ENERGY.DATA ENDOF
12 OF GAIN 8 0 FIX.FORMAT
18 YPOS GOTO.XY 18 SPACES
18 YPOS GOTO.XY STAT 6 . 8 3 FIX.FORMAT ENDOF
ENDCASE
"NULL VAL$ ":=
;
;
: EDIT.WINDOW \ Controls the editing functions
4 17 GOTO.XY ." Press <ESC> when finished. 
2 YPOS :=
BEGIN
27 XPOS :=
YPOS NUM$VAL 1 + > IF 2 YPOS := THEN
MESSAGE.CASE
YPOS 6 = STAT 1 3 < AND IF YPOS 1 + YPOS := THEN
XPOS YPOS GOTO.XY
EDIT.ENTRY
EDIT.CASE
YPOS 1 + YPOS :=
STACK.CLEAR
AGAIN
ONERR:
?ERROR# 0 <> IF ?ERROR# ERROR THEN
4 20 GOTO.XY ." Are you finished? (Y or N): 
Y,OR,N YN? " N" == IF
MYSELF
ELSE
RESTORE.FUNCTION.KEYS
0. 0.14 1. 1. RESTORE.VIDEO(AUTO)
PREVIOUS.WINDOW
" .SCAN" "TERM
THEN
;
MENU.INIT \ Starts the menu function
" WHITE" FORE.COLOR ":=
." Set which register " PROMPT
SCAN.VALUE.WINDOW
PRINT.HEADINGS
EDIT.WINDOW

; VIEW.LABEL \ Adds labels for screen output
NORMAL.COORDS 14 LABEL.COLOR
.5 .055 POSITION TERM? IF " Mass (m/z)" ELSE
" Electron Energy (eV)" THEN LABEL
270 LABEL.DIR
.05 .75 POSITION " Intensity " LABEL
0 LABEL.DIR
.08 .97 POSITION " Scale: " LABEL
.44 .97 POSITION " Sensitivity:" LABEL
.58 .97 POSITION SENSITIVE LABEL
.67 .97 POSITION TERM? IF " eV:" .69 ELSE " Mass:" .71 THEN LABEL
6 2 FIX.FORMAT
.97 POSITION STAT [ 4 ] "." LABEL
-1 4 FIX.FORMAT
WORLD.COORDS

; PLOT.LABEL \ Adds additional labeling for plotted output
NORMAL.COORDS 14 LABEL.COLOR
.02 .025 POSITION " Repevd Group NCSU" LABEL
.89 .025 POSITION "DATE LABEL
.22 .97 POSITION " Filename: " LABEL
.32 .97 POSITION REG " .NAME" CAT+ LABEL
.22 .94 POSITION REG " .COMMENT" CAT+ LABEL
VIEW.LABEL

; EXPAND.LIMITS \ Sets the expanded limits
EXSC EQUIV> SC-TOK EXSCMIN EQUIV> SCMIN-TOK
EXLM EQUIV> LM-TOK EXHM EQUIV> HM-TOK

; NORMAL.LIMITS \ Sets the full viewing limits
SC EQUIV> SC-TOK SCMIN EQUIV> SCMIN-TOK 1 ILOW := PTS# IHI :=

; CHECK.LIMITS
1 EXPAND.VALUE = IF
EXPAND.LIMITS
ELSE
NORMAL.LIMITS
THEN

;
DATA.VU  \ Plots the grids and tick marks for plot
NORMAL.COORDS
0.00 0.140 VUPORT.ORIG
1.00 1.00 VUPORT.SIZE
HORIZONTAL AXIS.FIT.OFF GRID.OFF
VERTICAL AXIS.FIT.OFF GRID.OFF
.16 .14 AXIS.ORIG
.84 .78 AXIS.SEIZE
.012 .008 TICK.SIZE
WORLD.COORDS
LM-TOK HM-TOK HORIZONTAL WORLD.SET
SCMIN-TOK SC-TOK VERTICAL WORLD.SET
1.0 1.0 TICK.JUST
HORIZONTAL NO.LABELS
VERTICAL NO.LABELS
AXIS.VALUE 1 = IF
HM-TOK SC-TOK AXIS.POINT XY_AXIS.PLOT THEN
HORIZONTAL 1 2 LABEL.POINTS LABEL.SCALE.OFF
VERTICAL 0 2 LABEL.POINTS
NORMAL.COORDS .15 .97 LABEL.SCALE.POINT WORLD.COORDS
0.0 0.0 TICK.JUST
AXIS.VALUE 1 = IF
LM-TOK SCMIN-TOK AXIS.POINT XY_AXIS.PLOT THEN
WORLD.COORDS
;

VU
9 AXIS.COLOR
DATA.VU
1 AXIS.VALUE = IF VIEWLABEL THEN
;

VIEW
EQUIV> Y-TOK
CHECK.LIMITS
MAX.CHECK
VU
X-AXIS SUB[ ILOW , IHI ILOW - 1 + ]
Y-TOK SUB[ ILOW , IHI ILOW - 1 + ]
PEN.COL COLOR 12 PEN.COL :=
XY.DATA.PLOT
;

PLOT
.* Plot which Register " PROMPT REG "EXEC EQUIV> Y-TOK
HP7470 DEVICE.INIT 6 PLOTTER.PENS
.* Select pen color ( 1 thru 6)" #INPUT PEN.COL := PEN.COL COLOR
DATA.VU 1 AXIS.VALUE = IF 9 AXIS.COLOR PLOT.LABEL THEN
CHECK.LIMITS
X-AXIS SUB[ ILOW , IHI ILOW - 1 + ]
Y-TOK SUB[ ILOW , IHI ILOW - 1 + ]
XY.DATA.PLOT
GRAPH.OUTPUT
IBM.GRAPhICS DEVICE.INIT
NORMAL.COORDS 0.00 .140 VUPORT.ORIG
1.00 1.00 VUPORT.SIZE WORLD.COORDS
;

SCREEN.VU  \ Plots spectrum on screen.
12 PEN.COL :=
.* View which register " PROMPT REG "EXEC VIEW
;

AXIS.TYPE
{VIEW} SCREEN.CLEAR GREEN INTEN MIX FOREGROUND 1 EXPAND.VALUE =
IF
." EXP" ELSE
." NML" THEN
PREVIOUS.WINDOW
;

AXIS.SET
0 EXPAND.VALUE = IF
TERM? IF ." Enter the Low Mass " #INPUT EXLM :=
CR ." Enter the High Mass " #INPUT EXHM := ELSE
CR ." Enter the Low Energy " #INPUT EXLM :=
CR ." Enter the High Energy " #INPUT EXHM := THEN
CR ." Enter the Low Intensity " #INPUT EXSCMIN :=
CR ." Enter the High Intensity " #INPUT EXSC :=
1 EXPAND.VALUE := EXPAND.LIMITS
ELSE
0 EXPAND.VALUE := NORMAL.LIMITS
THEN
AXIS.TYPE
;

CURSOR
12000 KEY.DELAY
NORMAL.COORDS
.8 .975 READOUT>POSITION
WORLD.COORDS
ARRAY.READOUT
;

CSR.VAL \ Returns the value of the Cursor
6 2 FIX.FORMAT
?CURSOR SWAP .
." (" 8 5 FIX.FORMAT "." )
-1 4 FIX.FORMAT
;

PRINT.CURSOR
OUT>PRINTER
REG ".NAME" CAT+ "TYPE "
CSR.VAL CR
CONSOLE
;

PRINT.COMMENT
OUT>PRINTER
REG ".NAME" CAT+ "TYPE ." REG ".COMMENT" CAT+ "TYPE CR
CONSOLE
;

PRE.CHECK
." many data points required! Calling scan setup." MENU.INIT MYSELF
THEN
;

; SCAN  \\ This function actually collects data from the C-50
STACK.CLEAR
  ." Scan which register " PROMPT
PTS# REAL RAMP BECOMES> Y-TOK PTS# REAL RAMP BECOMES> INTENSITY
SET.MASS.RANGE PRE.CHECK
  " .DA" "TERM D/A.INIT
STAT [ 4 ]
TERM? IF " ENERGY" ELSE " MASS" THEN " .DATA" CAT+
STAT [ 3 ] EQUIV> HM-TOK
TERM? IF CR ." Scanning (Mass) !" ELSE
  ." Scanning (electron energy) !" THEN
VU
AXIS.BUFFER LINE.BUFFER.ON
  " .DA" "TERM D/A.INIT
TERM " .DATA CONVERT" "CAT XEQ.FUNCTION " :=
  0 Y-TOK :=
  X-AXIS SUB[ 1 , PTS# ] X-ARRAY SUB[ 1 , PTS# ] :=
RESCAN 0 DO
  ." I 1 +
  X-ARRAY [ 1 ] DUP XEQ.FUNCTION "EXE& DUP INTENSITY [ 1 ] :=
POSITION
PTS# 1 + 2 DO
  X-ARRAY [ I ] DUP
  XEQ.FUNCTION "EXE&
  DUP INTENSITY [ I ] :=
  DUP SC-TOK > IF DROP SC-TOK THEN
DRAW.TO
LOOP
  Y-TOK INTENSITY + Y-TOK :=
ERASE.LINES
LOOP
LINE.BUFFER.OFF
Y-TOK RESCAN / REG "EXEC SUB[ 1 , PTS# ] :=
0 0 BECOMES> Y-TOK BECOMES> INTENSITY
VUPORT.CLEAR
NORMAL.LIMITS 0 EXPAND.VALUE := AXIS.TYPE
REG "EXEC VIEW

;  \\ Data Storage and Retrieval Routines.
: NEW.DIRECTORY.IN
  ." The current input directory is: " DIRECTORY.IN "TYPE ." ." CR
  ." Please type in the new directory name. " "INPUT DIRECTORY.IN ":= CR

: NEW.DIRECTORY.OUT
  ." The current output directory is: " DIRECTORY.OUT "TYPE ." ." CR
  ." Please type in the new directory name. " "INPUT DIRECTORY.OUT ":= CR

: COPY.FILE
  ." Source File " PROMPT ?DROP
REG "EXEC
STAT
REG " .NAME" CAT+
REG " .COMMENT" CAT+
  ." Target File " PROMPT ?DROP
REG " .COMMENT" CAT+ ":=
REG " .NAME" CAT+ :=
STAT :=
REG "EXEC :=
;
: CHECK.FILE
DIRECTORY.OUT "SWAP "CAT TERM? IF " .MAS" ELSE " EE" THEN
"CAT" DEFER> FILE.OPEN
FILE.CLOSE
BELL CR ." FILE ALREADY EXISTS! Do you want to write over it? (Y or N) " Y.OR.N YN? EXIT.SAVE ":=
ONERR: EXIT
;

: SAVE.DATA.NAME
" Y" EXIT.SAVE ":=
CR ." Save which Register, "
PROMPT
." Enter file name : " "INPUT "DUP NAME ":=
CHECK.FILE
EXIT.SAVE " N" ":= IF MYSELF THEN
;

: FULL.DISK.WARNING
DIRECTORY.OUT "DUP "DUP
" C:" "WITHIN IF EXIT THEN
" A:" "WITHIN IF 340425 ELSE 713161 THEN
" *:" "CAT DEFER> FILE.SIZES DROP < IF
." The disk is full. Insert a fresh disk and type any key when ready. " CR
PKEY THEN
;

: SAVE.DATA
SAVE.DATA.NAME
EXEC A.NAME CAT+ ":= CR
." Comments : " "INPUT
REG " .NAME" CAT+ ":= CR
REG " .NAME" CAT+ NAME ":=
DIRECTORY.OUT NAME "CAT
TERM? IF " .MAS" ELSE " EE" THEN
"CAT NAME ":=
FULL.DISK.WARNING

FILE.TEMPLATE
1 COMMENTS
INTEGER DIM[ LEN ] SUBFILE
REAL DIM[ PTS# ] SUBFILE
END

NAME DEFER> FILE.CREATE
NAME DEFER> FILE.OPEN
REG " .COMMENT" CAT+ 1 >COMMENT
1 SUBFILE STAT SUB[ 1 , LEN ] ARRAY>FILE
2 SUBFILE REG "EXEC SUB[ 1 , PTS# ] ARRAY>FILE
FILE.CLOSE
CR
;

: INPUT.FILE
STAT [ 1 ] CASE
2 OF 0.1 RESOL :=
PTS# RESOL * STAT [ 2 ] + STAT [ 3 ]:= ENDOF
ENDCASE ;
: OPEN.FILE.ONLY
"DUP DIRECTORY.IN "SWAP "CAT TERM? IF " .MAS" ELSE " .EE" THEN
"CAT NAME ":=
REG " .NAME" CAT+ ":=
NAME DEFER> FILE.OPEN
1 COMMENT> REG " .COMMENT" CAT+ ":=
1 SUBFILE FILE>UNNAMED.ARRAY DUP [ 1 ] STAT [ 1 ] :=
STAT SUB[ 1 , LEN ] :=
INPUT.FILE
2 SUBFILE REG "EXEC SUB[ 1 , PTS# ] FILE>ARRAY
FILE>CLOSE
NORMAL.LIMITS
STAT [ 5 ] CASE
64 OF " Low" SENSITIVE " := ENDOF
192 OF " Med" SENSITIVE " := ENDOF
128 OF " High" SENSITIVE " := ENDOF
ENDCASE
CR ." File : 
REG " .NAME" CAT+ "TYPE CR
REG " .COMMENT" CAT+ "TYPE CR
CR

: OPEN.FILE
CR
." Retrieve into which Register, "
PROMPT
." File name please ? " INPUT
OPEN.FILE.ONLY
ONERR: ." Can't open that file! Type any key to continue."
BELL PCKEY ?DROP DROP
?FILE.OPEN IF FILE>CLOSE THEN

: DIRECTORY.INPUT
" DIR " DIRECTORY.IN "CAT TERM? IF " *.MAS" ELSE " *.EE" THEN
CAT+

: DIRECTORY.OUTPUT
" DIR " DIRECTORY.OUT "CAT TERM? IF " *.MAS" ELSE " *.EE" THEN
CAT+
: STATUS
  (OTHER) SCREEN.CLEAR
  (BORDER)
  ." Which Register, " PROMPT
  ." File name : " REG ".NAME" CAT+ "TYPE CR
  ." Comments : " REG ".COMMENT" CAT+ "TYPE CR
  STAT [ 1 ] CASE
    0 OF." Fixed (100) point MASS format." ENDOF
    1 OF." Fixed resolution ENERG format." ENDOF
    2 OF." Fixed (0.1 amu increment MASS format." ENDOF
    3 OF." All variable MASS format, # pts, " PTG# .." , resolution, " RESOL .." ." ENDOF
    4 OF." All variable ENERGY format, # pts, " PTS# .." , resolution, " RESOL .." ." ENDOF
  ENDCASE
  CR
    64 OF." Low" "TYPE ENDOF
    192 OF." Med" "TYPE ENDOF
    128 OF." High" "TYPE ENDOF
  ENDCASE CR
  ." Repeat number :" STAT [ 7 ] . CR

: ARRAY.STATUS
  SCREEN.CLEAR
  ." Reg Name  Type Range  Resol.  Comment" CR
  LAST.LETTER 1 + FIRST.LETTER DO
    " R" I ":" "CAT "CMFSS REG ":=
    INPUT.FILE
    SPACE REG "TYPE ". " - 
    REG " NAME" CAT+ "TYPE
    4 1 FIX.FORMAT
    6 4 FIX.FORMAT RESOL.
    3 SPACES REG ".COMMENT" CAT+ "TYPE CR
    I 6 / I 6.0 / = IF ." <Press Any key to Continue>" PCKEY CR
    ." Reg Name  Type Range  Resol.  Comment" CR THEN
    LOOP " R" REG# ":," "CAT "CMFSS REG ":=

\ ----------- Mass Spectra Peak Location Routines -----------

: PEAK.SET
  CR ." How many peaks to monitor (100 or less) ?" #INPUT N.PEAKS := CR
  CR ." Enter the peak masses: "
  N.PEAKS 1 + 1 DO
    ." [ i .. ]" #INPUT DUP PEAK.MASS [ I ] := CR
  LOOP
  0 ERROR.PK :=
  FLATTEN?

: PEAK.POSITION.ARRAY
  REG "EXEC SUB[ PEAK.MASS [ I ] INDEX 0.5 RESOL / - , 1 RESOL / ]

: PEAK.POSITION.FIND
PEAK.MASS [ I ] INDEX COU := \ Note: I is an increment FUNCTION not a
COU 0.6 RESOL / + 1 + \ VARIABLE! It has different values in
COU 0.6 RESOL / - 0 + DO \ the inner loop; (see ASYST manual).
  I 1 + HI := ARRAY.PTS HI < IF ARRAY.PTS HI := THEN
  I 1 - LO := 0 LO > IF 0 LO := THEN
  REG "EXEC [ HI ] REG "EXEC [ I ] <=
  REG "EXEC [ LO ] REG "EXEC [ I ] <= AND
  REG "EXEC [ I ] REG "EXEC [ COU ] >= AND IF
  I COU :=
  THEN
  LOOP
  COU PTS# > IF
  ." Out of Range." 1 ERROR.PK :=
  1 COU :=
  THEN
PEAK.MASS [ I ] INDEX 0.6 RESOL / + 1 + COU =
PEAK.MASS [ I ] INDEX 0.6 RESOL / - 0 + COU = OR IF
PEAK.MASS [ I ] INDEX COU := ." Peak not found." 1 ERROR.PK :=
  THEN

;

: FILE.PEAKS.MAIN_ROUTINE
OPEN.FILE.ONLY
FLATTEN
-1 5 FIX.FORMAT
COUNTER1 1 + COUNTER1 :=
CR ." Set Mass    Act Mass   Intens" CR
X-AXIS SUB[ 1 , PTS# ] X-ARRAY SUB[ 1 , PTS# ] :=
N.PEAKS 1 + 1 DO
  COUNTER 1 = IF
    1 ERROR.PK = IF -10.0 0 ERROR.PK := ELSE REG "EXEC [ COU ] THEN
  ELSE
    PEAK.MASS [ I ] INDEX COU :=
    REG "EXEC [ COU ]
    THEN
    PEAK.DATA [ COUNTER1 , I ] :=
    X-ARRAY [ COU ] REAL.MASS [ COUNTER1 , I ] :=
    5 1 FIX.FORMAT PEAK.MASS [ I ] . 5 SPACES X-ARRAY [ COU ] . 5 SPACES
    8 6 FIX.FORMAT PEAK.DATA [ COUNTER1 , I ] . CR
    LOOP CR
    REG " .NAME" CAT+ " DUP SPECTRA.NAMES "[ COUNTER1 ] ":= "TYPE CR
    REG " .COMMENT" CAT+ SPECTRA.COMMENTS "[ COUNTER1 ] ":=

;

: FILE.PEAKS
0 COUNTER1 :=
."
" Do you want the peak search function? (Y or N)" Y.OR.N
" Y" YN? " = IF 1 COUNTER := ELSE 0 COUNTER := THEN CR
BEGIN
."
" File name please? " "INPUT
FILE.PEAKS.MAIN_ROUTINE
."
" Would you like to look at another file? (Y or N)" Y.OR.N YN? " N" =
IF
EXIT
THEN CR
AGAIN
STACK.CLEAR
;
BEGIN FALSE ." MASS VALUES "
ITER 1 = IF
 40 SPACES
 1 MINCOL := 1 MAXCOL :=
ELSE
  MAXCOL 1 + MINCOL := 4 MAXCOL + MAXCOL :=
THEN
 MAXCOL N.PEAKS > IF
 N.PEAKS MAXCOL := TRUE
THEN
7 2 FIX.FORMAT
MAXCOL 1 + MINCOL DO PEAK.MASS [ I ] ." " LOOP CR CR
COUNTER1 1 + 1 DO
 2 0 FIX.FORMAT I . 2 SPACES 6 4 FIX.FORMAT
SPECTRA.NAMES "[ I ] "TYPE
 14 ?REL.COL - SPACES
ITER 1 = IF
 SPECTRA.COMMENTS "[ I ] "TYPE
 66 ?REL.COL - SPACES
THEN
 MAXCOL 1 + MINCOL DO
 8 4 FIX.FORMAT PEAK.DATA [ J , I ] ." "
 5 1 FIX.FORMAT REAL.MASS [ J , I ] ." "
 LOOP CR
 LOOP 6 4 FIX.FORMAT CR CR CR CR
ITER 1 + ITER :=
UNTIL
CONSOLE
;

: PLOT.FILE.CREATES ASCII text data files.
." Enter file name: " "INPUT "DUP
REG ".NAME" CAT+ ":= CR
DIRECTORY.OUT "SWAP "CAT " .DAT" "CAT NAME ":= 
FULL.DISK.WARNING

CONSOLE.OFF
NAME DEFER> OUT>FILE
TAB TAB
7 1 FIX.FORMAT
N.PEAKS 1 + 1 DO PEAK.MASS [ I ] . TAB LOOP CR
9 5 FIX.FORMAT
COUNTER1 1 + 1 DO
 SPECTRA.NAMES "[ I ] "TYPE TAB
SPECTRA.COMMENTS "[ I ] "TYPE TAB
N.PEAKS 1 DO
 PEAK.DATA [ J , I ] . TAB
 LOOP PEAK.DATA [ I , N.PEAKS ] . CR
 LOOP
OUT>FILE.CLOSE
CONSOLE
8 4 FIX.FORMAT
ONERR: OUT>FILE.CLOSE
CONSOLE ." Can't create that file! Type any key to continue "
PKKEY ?DROP DROP
?FILE.OPEN IF FILE.CLOSE THEN
;
\ ------------------ Batch processing routines ------------------

: CREATE.FILE
  ROOT.NAME
  I " 0000" "," "CAT "CMFSS 4 "RIGHT
  "CAT

: SPECTRUM.FILE \ Creates ASCII text plot files.
  "DUP OPEN.FILE.ONLY
  DIRECTORY.OUT "SWAP "CAT " .PLT" "CAT NAME ":=
  FULL.DISK.WARNINO

  CONSOLE.OFF
  NAME DEFER> OUT>FILE
  X-AXIS SUB[ 1 , PTS# ] X-ARRAY SUB[ 1 , PTS# ] :=
  TAB REG " .NAME" CAT+ "TYPE CR
  TAB REG " .COMMENT" CAT+ "TYPE CR
  ." Mass (m/z)" TAB ." Intensity (arb.)" TAB CR
  PTS# 1 + 1 DO
    6 2 FIX.FORMAT X-ARRAY [ I ] . TAB 7 4 FIX.FORMAT REG "EXEC [ I ] . CR
  LOOP CR
  OUT>FILE.CLOSE
  CONSOLE
  0 4 FIX.FORMAT

  ONERR: OUT>FILE.CLOSE
    CONSOLE ." Can't create that file! Type any key to continue "
    PCKEY ?DROP DROP
    ?FILE.OPEN IF FILE.CLOSE THEN

  : AUTO.OPEN
  FINISH 1 + START DO I COUNTER2 :=
  CREATE.FILE
  AUTO.COMMAND "EXEC
  LOOP

  ONERR: ." Can't open that file! Type <ESC> to end, <CR> to retry same file,"
  CR ." or press <SPACE> to advance to the next file."
  BEGIN
    BELL PCKEY ?DROP CASE
      13 OF COUNTER2 START := TRUE ENDOF
      27 OF EXIT TRUE ENDOF
      32 OF COUNTER2 1 + START := TRUE ENDOF
      FALSE
    ENDCASE
    UNTIL
    ?FILE.OPEN IF FILE.CLOSE THEN MYSELF

  : LOAD.REGISTERS
  COUNTER2 ASCII" REG ":=
  OPEN.FILE.ONLY
  COUNTER2 1 + COUNTER2 :=
  ;
: AUTOMATIC_LOAD_REGISTERS
  ." Retreive into which register, " PROMPT
  ." Give the root name string. " "INPUT ROOT.NAME " := CR
  ." Give the start file number. " #INPUT START := CR
  ." Give the finishing file number. " #INPUT FINISH := CR
  ." Give the starting register, " PROMPT REG# COUNTER2 := CR
  " LOAD_REGISTERS" AUTO.COMMAND ":=
  AUTO.OPEN

;

: AUTOMATIC_PEAK_FINDER
  0 COUNTER1 :=
  ." Do you want the peak search function? (Y or N)" Y.OR.N
  " Y" YN? " := IF 1 COUNTER := ELSE 0 COUNTER := THEN CR
  ." Give the root name string. " "INPUT ROOT.NAME " := CR
  ." Give the start file number. " #INPUT START := CR
  ." Give the finishing file number. " #INPUT FINISH := CR
  " FILE_PEAKS.MAIN_ROUTINE" AUTO.COMMAND ":=
  AUTO.OPEN

;

: AUTOMATIC_PLOT_MAKER
  0 COUNTER1 :=
  " Y" YN? " := IF 1 COUNTER := ELSE 0 COUNTER := THEN CR
  ." Give the root name string. " "INPUT ROOT.NAME " := CR
  ." Give the start file number. " #INPUT START := CR
  ." Give the finishing file number. " #INPUT FINISH := CR
  " SPECTRUM.FILE" AUTO.COMMAND ":=
  AUTO.OPEN

;
\------------- Window Routines ------------
: RETURN
  0 .14 1.1. RESTORE.VIDEO(AUTO)
  PREVIOUS.WINDOW
  RETURN.TO "EXEC

;

: CORNER
  {AXIS} AXIS.VALUE 1 = IF ." Y" ELSE ." N" THEN
  {REGISTER} REG#

;

: OPTIONS_FTNS
  ." <Alt-7> AUTO PLOT <Sft-7> AUTO PEAK <Alt-9> NW OUT DIR <Sft-9> NW IN DIR" CR

;

: OPTION_KEYS
  TERM " .SCAN" "CAT RETURN TO " :=
  F1 FUNCTION.KEY.DOES PEAK.SET
  F2 FUNCTION.KEY.DOES PLATTEN?
  F3 FUNCTION.KEY.DOES PLATTEN
  F4 FUNCTION.KEY.DOES FILE.PEAKS
  F5 FUNCTION.KEY.DOES PEAK.DATA.ARRAY.PRINT
  F6 FUNCTION.KEY.DOES PLOT.FILE.CREATE
  F7 FUNCTION.KEY.DOES OPTIONS_FTNS
  F8 FUNCTION.KEY.DOES COPY.FILE
  F10 FUNCTION.KEY.DOES RETURN

  F7 ALT FUNCTION.KEY.DOES AUTOMATIC.PLOT.MAKER
  F7 SHIFT FUNCTION.KEY.DOES AUTOMATIC.PEAK.FINDER
  F9 ALT FUNCTION.KEY.DOES NEW.DIRECTORY.OUT
  F9 SHIFT FUNCTION.KEY.DOES NEW.DIRECTORY.IN

;
OPTION.ANALYSIS
TV
CLEAR.FUNCTION.KEYS
{BOTTOM} SCREEN.CLEAR
RED GREEN MIX FOREGROUND
." <1>PORR SL <2>ST FLT <3>FLT <4> FILE IN <5>LPT "
." <6> FILE OUT <7>ALT <8>CPY <10>"
GREEN BLUE MIX FOREGROUND ." RTN"
CORNER
{OTHER} SCREEN.CLEAR
{BORDER}
OPTION.KEYS
;

DISK.FUNCTION.KEYS
TERM " .SCAN" " CAT RETURN TO ":-
F1 FUNCTION.KEY.DOES SAVE.DATA
F2 FUNCTION.KEY.DOES OPEN.FILE
F3 FUNCTION.KEY.DOES DIRECTORY.INPUT
F4 SHIFT FUNCTION.KEY.DOES DIRECTORY.OUTPUT
F5 FUNCTION.KEY.DOES NEW.DIRECTORY.OUT
F6 FUNCTION.KEY.DOES NEW.DIRECTORY.IN
F7 FUNCTION.KEY.DOES STATUS
F8 FUNCTION.KEY.DOES AUTOMATIC.LOAD. REGISTERS
F9 FUNCTION.KEY.DOES ARRAY.STATUS
F10 FUNCTION.KEY.DOES RETURN
;

DISK.FUNCTION
TV
CLEAR.FUNCTION.KEYS
{BOTTOM} SCREEN.CLEAR
TERM? IF WHITE ELSE GREEN THEN MIX FOREGROUND
." <1>SVE <2>LD <3>D IN <5>f<3>D OUT <4>WW OR <5>STAT "
." <6>AUT LD <7>ALL ST <10>"
RED BLUE MIX FOREGROUND ." RTN"
CORNER
{OTHER} SCREEN.CLEAR
{BORDER}
DISK.FUNCTION.KEYS
;

SCAN.PTNS
." <Alt-7>CSR PRT <Alt-8>CMT PRT <Sft-2>CSR VAL <Sft-3>AXIS?" CR
." <Sft-4>FLATTEN <Sft-5>SET AXS <Sft-6>MAX? " CR
;

SCAN.KEYS
" MAIN.DISPLAY.KEYS" RETURN.TO ":-
F1 FUNCTION.KEY.DOES VRSPORT.CLEAR
F2 FUNCTION.KEY.DOES CURSOR
F3 FUNCTION.KEY.DOES SCAN
F4 FUNCTION.KEY.DOES MENU.INIT
F5 FUNCTION.KEY.DOES SCREEN.VU
F6 FUNCTION.KEY.DOES PLOT
F7 FUNCTION.KEY.DOES OPTION.ANALYSIS
F8 FUNCTION.KEY.DOES SCAN.PTNS
F9 FUNCTION.KEY.DOES DISK.FUNCTION
F10 FUNCTION.KEY.DOES RETURN

F2 SHIFT FUNCTION.KEY.DOES CSR.VAL
F7 ALT FUNCTION.KEY.DOES PRINT.CURSOR
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F8 ALT FUNCTION.KEY.DOES PRINT.COMMENT
F3 SHIFT FUNCTION.KEY.DOES AXIS?
F4 SHIFT FUNCTION.KEY.DOES FLATTEN!
F5 SHIFT FUNCTION.KEY.DOES AXIS.SET
F6 SHIFT FUNCTION.KEY.DOES MAX?
CORNER AXIS.TYPE
{WORKSPACE}

; MASS.SCAN
CLEAR.FUNCTION.KEYS
" MASS" TERM ":=" " BLUE" BACK.COLOR ":= 12 NUM#VAL :=
{BOTTOM} SCREEN.CLEAR
RED BLUE MIX FOREGROUND ." <1>CLR <2>CSR <3>SCN <4>"
RED MIX FOREGROUND ." ST UP "
RED BLUE MIX FOREGROUND ." <5>VU <6>PLT <7>"
RED GREEN MIX FOREGROUND ." PEAK "
RED BLUE MIX FOREGROUND ." <8>ALT "
RED BLUE MIX FOREGROUND ." <9>"
WHITE MIX FOREGROUND ." DISK"
RED BLUE MIX FOREGROUND ." <10>"
GREEN BLUE MIX FOREGROUND ." RTN"
SCAN.KEYS

; ENERGY.SCAN
CLEAR.FUNCTION.KEYS
" ENERGY" TERM ":=" " RED" BACK.COLOR ":= 12 NUM#VAL :=
{BOTTOM} SCREEN.CLEAR
BLUE INTEN MIX FOREGROUND ." <1>CLR <2>CSR <3>SCN <4>"
RED MIX FOREGROUND ." ST UP "
BLUE INTEN MIX FOREGROUND ." <5>VU <6>PLT <7>"
RED GREEN MIX FOREGROUND ." PEAK "
BLUE MIX FOREGROUND ." <8>ALT "
BLUE MIX FOREGROUND ." <9>"
GREEN MIX FOREGROUND ." DISK"
BLUE MIX FOREGROUND ." <10>"
GREEN MIX FOREGROUND ." RTN"
SCAN.KEYS

; MAIN.DISPLAY.MENU
CLEAR.FUNCTION.KEYS
{BOTTOM} SCREEN.CLEAR
RED BLUE MIX FOREGROUND ." <1>MASS SCAN "
GREEN MIX FOREGROUND ." <2>ENERGY SCAN" 35 SPACES BLUE MIX FOREGROUND ." <10>EXIT"

; MAIN.DISPLAY.KEYS
MAIN.DISPLAY.MENU
F1 FUNCTION.KEY.DOES MASS.SCAN
F2 FUNCTION.KEY.DOES ENERGY.SCAN
F10 FUNCTION.KEY.DOES EXITING
{WORKSPACE}

;
FUNCTION.INITIALIZE
STACK.CLEAR
STAT [ 4 ] ENERGY.DATA
SENSITIVITY
GAIN
;

RESTART
STORE.FUNCTION.KEYS
CLEAR.FUNCTION.KEYS
INITIAL.VALUES MASS.INITIAL.VALUES SCREEN.CLEAR
FUNCTION.INITIALIZE
18 GRAPHICS.DISPLAY.MODE
GRAPHICS.DISPLAY
TEXT.CURSOR.ON
{BOTTOM}
RS232 POL.MODE
MAIN.DISPLAY.KEYS
1 AXIS.VALUE := (AXIS) " Y" PREVIOUS.WINDOW
{REGISTER} 3 0 FIX FORMAT REG# .
8 4 FIX FORMAT
PREVIOUS.WINDOW
;

INIT
EXP.MEM> R1 ARRAY.PTS REAL RAMP BECOMES> R1
EXP.MEM> R2 ARRAY.PTS REAL RAMP BECOMES> R2
EXP.MEM> R3 ARRAY.PTS REAL RAMP BECOMES> R3
EXP.MEM> R4 ARRAY.PTS REAL RAMP BECOMES> R4
EXP.MEM> R5 ARRAY.PTS REAL RAMP BECOMES> R5
EXP.MEM> R6 ARRAY.PTS REAL RAMP BECOMES> R6
EXP.MEM> R7 ARRAY.PTS REAL RAMP BECOMES> R7
EXP.MEM> R8 ARRAY.PTS REAL RAMP BECOMES> R8
EXP.MEM> R9 ARRAY.PTS REAL RAMP BECOMES> R9
EXP.MEM> R10 ARRAY.PTS REAL RAMP BECOMES> R10
EXP.MEM> R11 ARRAY.PTS REAL RAMP BECOMES> R11
EXP.MEM> R12 ARRAY.PTS REAL RAMP BECOMES> R12
EXP.MEM> R13 ARRAY.PTS REAL RAMP BECOMES> R13
EXP.MEM> R14 ARRAY.PTS REAL RAMP BECOMES> R14
EXP.MEM> R15 ARRAY.PTS REAL RAMP BECOMES> R15
EXP.MEM> R16 ARRAY.PTS REAL RAMP BECOMES> R16
EXP.MEM> R17 ARRAY.PTS REAL RAMP BECOMES> R17
EXP.MEM> R18 ARRAY.PTS REAL RAMP BECOMES> R18
EXP.MEM> R19 ARRAY.PTS REAL RAMP BECOMES> R19
EXP.MEM> R20 ARRAY.PTS REAL RAMP BECOMES> R20
EXP.MEM> X-ARRAY ARRAY.PTS REAL RAMP BECOMES> X-ARRAY
EXP.MEM> PEAK DATA DIM[ 100 , 100 ]
UNNAMED ARRAY BECOMES> PEAK DATA
EXP.MEM> REAL MASS DIM[ 100 , 100 ]
UNNAMED ARRAY BECOMES> REAL MASS
LAST LETTER 1 + FIRST LETTER DO
" R" I ". " CAT "CMPSS REG ":=
0 REG "EXEC := 0 REG " .STAT" CAT+ :=
LOOP

RESTART
;
11.2 Sticking Probability Estimates

The sticking coefficient of gaseous species is an extremely important value when trying to estimate their contribution to film growth processes. However, this easily understood factor is difficult to measure in practice because of other intertwined effects, such as associative desorption, relaxation, and surface conditions. In addition, the sniffer tube length of this particular in-situ mass spectrometric detection system may hinder their detection, due to the sticking probability of deposition species.

In the design of the sniffer tube arrangement, care was taken to make sure that the pressure was low enough to create negligible gas-phase collisions. The mean free path is 44 cm, at a normal ion gauge operating pressure of $1.9 \times 10^{-6}$ Torr. The molecular flow regime in this tube is governed by gas molecules collisions with the walls. This means that particles traversing the tube undergo collisions which may remove them from the flow through deposition on the sniffer tube wall or conversion to another compound. Higher loss probability particles are removed at a faster rate, providing an effective filter that preferentially passes low loss probability species, such as SiH$_4$. Through a simple first-order analysis of wall collisions in the sniffer tube, it can be shown below that for high sticking coefficient species, the concentration of particles surviving the length of the sniffer tube drops. The proposed experiment presented below should determine the effect of the sniffer tube length on detectability. In addition, the experiment provides a method of determining the loss probability for each individual specie simultaneously in a deposition system.

This section describes a set of experiments to determine the loss probability of gaseous species used for deposition. First, a formulation is presented in which the effect of loss probability upon filtering of gaseous species will be presented. Then a discussion of this formula in creating an experiment to determine the loss probability is presented. Finally a discussion is presented to show how this information may be applied to
examining the effect on deposition of these species may be encountered, and how to redesign the sampling orifice to minimize selective filtration.

11.2.1 Loss Probability Formulation

As gas particles enter a small orifice into a narrow, pumped volume, they realize a flow regime called molecular gas flow, and their diffusion is governed by collisions with the chamber wall, not with each other. With each collision with the wall, there is a finite probability that the collision permanently removes the particle from the gas stream through some sort of reaction, say surface incorporation, energetic relaxation, or catalytic reaction into another gaseous specie. With the geometry of a narrow sniffer tube, tube length $\gg$ tube diameter, this loss term must be added to the transport equation. Figure 11.1 shows the effect of this mechanism upon the differential volume of gas particles traversing the tube. The assumptions made for this derivation are as follows:

![Diagram of gas particle flow in sniffer tube.](image)

Figure 11.1- Diagram of gas particle flow in sniffer tube.

1) $l \gg L$.
2) Isotropic particle velocity distribution.
3) Infinitely long tube.
4) End plates have $\beta = 0$.

where, $\beta$ is loss probability, $l$ is the mean free path, and $L$ is the characteristic dimension. The loss probability is made up of two terms, $\alpha$ the sticking probability, and $\zeta$ the non-incorporation reaction probability, $\beta = \alpha + \zeta$. Assumption 2 says that there are no fields affecting particle flow in the tube. This would only be a significant factor, if there was a thermal gradient along the length of the tube that affects surface reactions.
Assumptions 3 and 4 are for simplification of the analysis, in reality they could provide a measurable effect, but any effect would be seen as an offset in the data. Other terms to be defined for this analysis are, \( v \) - drift velocity, \( V \) - thermal velocity, \( r \) - tube radius, \( d \) - tube diameter = 2r, \( A \) - tube cross-sectional area = \( \pi r^2 \), \( D \) - Knudsen diffusion coefficient, = 1/3 VL, \( n \) - particle density, and \( C \) - molar concentration. The flux density components as shown in Fig. 11.1 are:

1) \( v \ A \ n \ C(x) \)
2) \(-D \ A \ n \frac{dC}{dx} \bigg|_{x + dx} \)
3) \( v \ A \ n \ C(x + dx) \)
4) \(-D \ A \ n \frac{dC}{dx} \bigg|_{x} \)
5) \( \frac{\beta n V}{4} C(x) 2 \pi r \ dx. \)

The differential continuity transport equation is,

\[
 n \ A \ dx \ \frac{dC}{dt} = -3) + 1) - 2) + 4) - 5) \tag{11.1}
\]

\[
 = -vAnC(x + dx) + vAnC(x) + DAn \frac{dC}{dx} \bigg|_{x + dx} - DAn \frac{dC}{dx} \bigg|_{x} - \alpha \frac{n V}{4} C(x) 2\pi r \ dx.
\]

For steady state conditions,

\[
 \frac{dC}{dt} = -v \frac{dC}{dx} + D \frac{d^2C}{dx^2} - \frac{V\pi r}{2A} C = 0 \tag{11.2}
\]

\[
 \frac{d^2C}{dx^2} - \frac{v}{D} \frac{dC}{dx} - \frac{V\pi r}{2AD} C = 0
\]

Substituting for the Knudsen Diffusion Coefficient \( D \),

\[
 \frac{d^2C}{dx^2} - \frac{3v}{LV} \frac{dC}{dx} - \frac{3\beta}{4Lr} C = 0 \tag{11.3}
\]

The characteristic equation for the homogeneous, linear, 2nd order, differential equation is,

\[
m^2 - \left( \frac{3v}{LV} \right) m - \frac{3\beta}{4Lr} = 0 \tag{11.4}
\]

\[
 \therefore \ C = \Psi_1 e^{m_1 x} + \Psi_2 e^{m_2 x} \tag{11.5}
\]
where,

\[ m_1 = \frac{3v}{2L} + \frac{1}{2} \sqrt{\left( \frac{3v}{L} \right)^2 + \left( \frac{3\beta}{Lr} \right)} \]  \hspace{1cm} (11.6)

(Physically unreal, \( \Psi_1 = 0 \))

\[ m_2 = \frac{3v}{2L} - \frac{1}{2} \sqrt{\left( \frac{3v}{L} \right)^2 + \left( \frac{3\beta}{Lr} \right)} \] \hspace{1cm} (\( \Psi_2 = C_0 \)) \hspace{1cm} (11.7)

Defining the characteristic length for infinitely long tubes as \( L = 2r \),

\[ m_2 = \frac{3}{4} \frac{v}{r} - \frac{1}{2} \sqrt{\left( \frac{3v}{2r} \right)^2 + \left( \frac{3\beta}{2r^2} \right)} \]  \hspace{1cm} (11.8)

For thermal velocity \( V \gg \) drift velocity \( v \),

\[ m_2 = -\frac{1}{2} \sqrt{\frac{3\beta}{2r^2}} = -\frac{1}{d} \sqrt{\frac{3\beta}{2}} \]  \hspace{1cm} (11.9)

\[ \therefore C(x) = C_0 \exp \left( \frac{x}{d} \sqrt{\frac{3\beta}{2}} \right) \]  \hspace{1cm} (11.10)

**11.2.2 Effect of Loss Probability on Throughput**

Equation 11.10 shows the relation between the loss probability as a function of tube length to be an exponential decay dependence. Figure 11.2 shows the effect of the varying tube length for different sticking coefficient species on the fractional decrease in concentration. The plot shows that for high sticking coefficients, the concentration drop is the greatest, a factor of 10 for a 1 cm tube change length for a sticking coefficient of 1.0. Even for a 1.0 sticking coefficient, some species still traverse the tube without collisions. It shows that there is a factor of 10 drop over about 2 cm change in tube length for a sticking coefficient of 0.1. Figure 11.3 shows the effect of sticking coefficient for a fixed tube length on the fractional decrease in concentration.
Figure 11.2 - Plot of fractional throughput as a function of tube length for different sticking coefficients.
Figure 11.3- Plot of the fractional throughput as a function of sticking coefficient for different sniffer tube lengths.

11.2.3 Loss Probability Experiment

As shown in the previous subsection, there is a logarithmic dependence of the tube length upon the concentration of species traversing the length of the tube. Based upon this behavior, an experiment is proposed to simultaneously measure the loss probabilities of all species produced in a glow discharge deposition system. The experiment is based upon the equation,

$$\ln\left(\frac{C}{C_0}\right) = -\frac{1}{d} \sqrt{\frac{3\beta}{2}} x$$  \hspace{1cm} (11.11)

where, $x$ is the length of the tube; it shows that the natural logarithm of the concentration is only a function of $d$ and $\beta$. Since $d$ is held constant and $x$ is varied, the slope of the
equation yields $\beta$. The spectrometer is a detector of the activated species, but the mass filter separates the species so that each mass signal provides information on individual species.

The basic experimental procedure is as follows. The shortest sniffer tube is installed over the mass spectrometer, and a measurement is made under all experimental conditions studied. Then the spectrometer is removed from the chamber and a longer segment is installed. The experiment is repeated until the tube length is long enough so that consecutive measurements show no more change in peak height. Once this final point is reached, it is assumed that the fraction of species passing through the sniffer tube is small enough to be neglected, and that the entire signal remaining is only due to non-reactive species with negligible loss probabilities. By subtracting this non-reactive signal contribution from the shorter tube length signals, the remaining component is from the reactive species. Plotting the difference signal as a function of natural logarithm of the concentration vs. the tube length, the slope yields the loss probability, $\beta$.

The loss probability is made up of a film incorporation loss term $\alpha$, and a surface reaction term $\zeta$. Perrin showed that $\zeta$ cannot necessarily be neglected, e.g. 60% of SiH$_3$ impinging upon a surface will recombine to form stable neutral compounds which desorb, such as Si$_2$H$_6$ [11.1]. Their experiments were performed at 1 Torr, while in the sniffer tube, the total pressure is on the order of $10^{-5}$ Torr. Such low pressure is 5 orders of magnitude lower than the maximum flux rates noted for $10^{-1}$ Torr; this difference implies that such loss by recombination would be negligible, : $\beta = \alpha$. However, there are experimental complications that must be addressed in order to derive the sticking coefficient, 1) the surface state may change between scans, 2) it may not be practical to filter out all reactive species with the tube length, 3) each mass signal may contain more than one reactive species.

Since the mass spectrometer is opened between scans, the surface of the tube is exposed to atmosphere. Therefore, it is important that the surface of the tube be maintained
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in as close a condition to the film surface state as possible. Before the scan is started, it is important to condition the walls. One method would be to first etch the silicon-coated walls with a hydrogen plasma for 30 minutes, then deposit the material of interest. One hour should sufficiently coat the walls so that changes in measurement time are negligible.

Some of the species sampled will have low enough $\alpha$, that their signal contribution will change on the order of the tube lengths employed. For those species it will not be practical for the tube to be lengthened enough to filter out the entire signal, meaning that the non-sticking species contribution cannot be entirely removed from the data. In those cases, it will be necessary to provide a curve fitting so that the curve shape may be determined, and $\alpha$ may be obtained from the slope. For those species, the fitting equation is

$$\frac{I_2 - I_1}{I_1 - I_0} = \chi = \frac{\exp\left(-\frac{x_2}{d}\sqrt{\frac{3\alpha}{2}}\right) - \exp\left(-\frac{x_1}{d}\sqrt{\frac{3\alpha}{2}}\right)}{\exp\left(-\frac{x_1}{d}\sqrt{\frac{3\alpha}{2}}\right) - \exp\left(-\frac{x_0}{d}\sqrt{\frac{3\alpha}{2}}\right)}.$$  \hspace{1cm} (11.12)

### 11.2.4 Design of Efficient Gas Collectors

The derivation shown in subsection 11.2.2 shows that a tube of the dimension of the current gas sniffer tube selectively filters a species with $\alpha$ of 0.05 by an order of magnitude, and $\alpha$ of 0.5 by almost two orders of magnitude. Therefore, it is important to be able to design a sampling orifice that will admit representative gas samples into the mass spectrometer while, keeping the pressure in the spectrometer in the $10^{-6}$ Torr level, and not filter reactive species from the sampled material. The best design for doing this is to place the mass spectrometer into the chamber where the sample would normally sit, but at the same time seal it from the high pressure of the reactor. For the larger diameter chamber described in Chapter 2, placing the filter into the chamber could be accomplished without serious compromise to the chamber flow patterns. Some quadrupole filters on the market today fit on a four inch diameter flange and have an outer diameter on the order of 6.3 cm.
In a 15.3 cm diameter chamber, a 8 cm tube should not provide a dramatic change in the flow of the system, compared with 1 and 3 in. sample holders.

### 11.3 Diffusion Coefficient Data Tables

Table 11.1 - Collision Integral \( \Omega \), and the viscosity temperature function based upon the Lennard-Jones Potential [11.2]

<table>
<thead>
<tr>
<th>( T^* = kT/\varepsilon_0 )</th>
<th>( \Omega )</th>
<th>( f_i(kT/\varepsilon_0) )</th>
<th>( kT/\varepsilon_0 )</th>
<th>( \Omega_s )</th>
<th>( f_s(kT/\varepsilon_0) )</th>
<th>( kT/\varepsilon_0 )</th>
<th>( \Omega_s )</th>
<th>( f_s(kT/\varepsilon_0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>2.785</td>
<td>0.1969</td>
<td>1.65</td>
<td>1.264</td>
<td>1.0174</td>
<td>4.0</td>
<td>0.9700</td>
<td>2.0719</td>
</tr>
<tr>
<td>0.35</td>
<td>2.623</td>
<td>0.2252</td>
<td>1.70</td>
<td>1.248</td>
<td>1.0453</td>
<td>4.1</td>
<td>0.9649</td>
<td>2.1090</td>
</tr>
<tr>
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† Hirschfelder, Curtiss, and Bird use the symbol \( T^* \) for \( kT/\varepsilon_0 \) and \( \Omega_s T^* \) for \( \Omega_s \). Bromley and Wilke use \( (kT/\varepsilon_0)^{5/3} V/W^{2/3} \) for \( f_i(kT/\varepsilon_0) \). More complete tables of these functions are given in the two references cited.
Table 11.2- Lennard-Jones Potentials as determined from viscosity data [11.2].

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<th>( a ) \text{ Å}</th>
<th>( \alpha / \beta ) °C</th>
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\[ h^* = \frac{H}{\sqrt{\pi \omega}}, \] where \( \omega \) is Avogadro's number.
\[ \alpha / \beta \] The potential \( \alpha \) was determined by quantum-mechanical formulas.
Table 11.3- Values of the collision integral $\Omega_d$ based on the Lennard-Jones potential [11.2].

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<th>$kT/\varepsilon_0$</th>
<th>$\Omega_d$</th>
<th>$kT/\varepsilon_0$</th>
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<td>0.8836</td>
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<td>1.75</td>
<td>1.125</td>
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<td>0.8740</td>
</tr>
<tr>
<td>0.45</td>
<td>2.184</td>
<td>1.80</td>
<td>1.116</td>
<td>4.3</td>
<td>0.8694</td>
</tr>
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<td>0.50</td>
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<td>1.85</td>
<td>1.105</td>
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<td>0.8632</td>
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<td>1.094</td>
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<td>1.95</td>
<td>1.084</td>
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<tr>
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<td>2.00</td>
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<td>0.7556</td>
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<td>2.8</td>
<td>0.9672</td>
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<td>2.9</td>
<td>0.9576</td>
<td>20.0</td>
<td>0.6640</td>
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<td>1.15</td>
<td>1.346</td>
<td>3.0</td>
<td>0.9490</td>
<td>30.0</td>
<td>0.6232</td>
</tr>
<tr>
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<td>0.9120</td>
<td>80.0</td>
<td>0.5352</td>
</tr>
<tr>
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<td>3.6</td>
<td>0.9053</td>
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<td>0.5256</td>
</tr>
<tr>
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<td>0.8998</td>
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<td>0.4644</td>
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<td>1.167</td>
<td>3.9</td>
<td>0.8888</td>
<td>400.0</td>
<td>0.4170</td>
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</table>


† Hirschfelder uses the symbols $T^*$ for $kT/\varepsilon_0$ and $\Omega_d^{(1,1)}$ in place of $\Omega_d$. 

-233-
Table 11.4- Estimation of properties of organometallic compounds [11.2].

APPENDIX H

ESTIMATION OF PROPERTIES OF ORGANOMETALLIC COMPOUNDS*

Few reliable data are available on the physical and thermodynamic properties of organometallic compounds, and few methods of estimating properties of such materials exist. An analogue technique recently suggested by Kapner for organometallic compounds containing tetravalent metals is summarized in this Appendix.†

The basis of the method is the organic analogue to the organometallic compound. This analogue is simply the identical compound, with all metallic atoms replaced by carbon, whether or not the organic compound does or does not exist as a stable entity. It is assumed, however, that the properties of any organic analogue are known or can be estimated by methods given in this book. The estimation of the properties of organometallics is then related to the corresponding property of the organic analogue. Only a few organometallic properties have been studied, but the concept may be expanded.

Table H-1. Estimation of Critical Temperatures for Organometallic Compounds, Direct Test of the Analogue Method

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analogue</th>
<th>θ</th>
<th>( T_b ), °C</th>
<th>( T_b ), °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl₄</td>
<td>CCl₄</td>
<td>0.6304</td>
<td>+57.3</td>
<td>524.0</td>
</tr>
<tr>
<td>GeCl₄</td>
<td>CCl₄</td>
<td>0.6304</td>
<td>+84.0</td>
<td>566.3</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>CCl₄</td>
<td>0.6304</td>
<td>+113.0</td>
<td>612.5</td>
</tr>
<tr>
<td>SICl₂F₄</td>
<td>CICl₂F₄</td>
<td>0.6313</td>
<td>+12.2</td>
<td>452.0</td>
</tr>
<tr>
<td>SICl₂F₃</td>
<td>CICl₂F₃</td>
<td>0.6321</td>
<td>-31.5</td>
<td>381.7</td>
</tr>
<tr>
<td>SICl₂F₂</td>
<td>CICl₂F₂</td>
<td>0.6339</td>
<td>-70.0</td>
<td>320.9</td>
</tr>
<tr>
<td>SIF₃</td>
<td>CF₃</td>
<td>0.6338</td>
<td>-94.8(s)</td>
<td>281.3</td>
</tr>
<tr>
<td>SiH₄</td>
<td>CH₄</td>
<td>0.587</td>
<td>-111.5</td>
<td>275.5</td>
</tr>
<tr>
<td>(CH₃)₂Si</td>
<td>(CH₃)₂C</td>
<td>0.641</td>
<td>+24.9</td>
<td>465.0</td>
</tr>
<tr>
<td>UCl₄</td>
<td>CCl₄</td>
<td>0.6304</td>
<td>+792.0</td>
<td>1689.6</td>
</tr>
</tbody>
</table>

Note: (s) = solid at 760 mm. \( T_b \) = normal boiling point of the organometallic.

* Most of this Appendix has been abstracted, with permission, from a paper by R. S. Kapner submitted to the AICHE J.

† The term organometallic also includes the inorganic type of compounds with tetravalent metallic atoms such as TiCl₄, SnH₄, GeH₄, etc.
Table 11.4- (continued) Estimation of properties of organometallic compounds [11.2].

<table>
<thead>
<tr>
<th>Table H-2. Van Laar Correlation of $b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van Laar Values</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$H$ = 59$^{(a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
</tr>
<tr>
<td>14</td>
</tr>
<tr>
<td>$C = 100^{(a)}$</td>
</tr>
<tr>
<td>$N = 85^{(b)}$</td>
</tr>
<tr>
<td>$O = 76^{(b)}$</td>
</tr>
<tr>
<td>$F = 55$</td>
</tr>
<tr>
<td>$Ne = 76$</td>
</tr>
<tr>
<td>$He = 105$</td>
</tr>
<tr>
<td>$175$</td>
</tr>
<tr>
<td>$60$</td>
</tr>
<tr>
<td>$50$</td>
</tr>
<tr>
<td>$17$</td>
</tr>
<tr>
<td>$Si = 155$</td>
</tr>
<tr>
<td>$P = 140$</td>
</tr>
<tr>
<td>$S = 125$</td>
</tr>
<tr>
<td>$Cl = 115$</td>
</tr>
<tr>
<td>$A = 144$</td>
</tr>
<tr>
<td>$Ti = 177.5^*$</td>
</tr>
<tr>
<td>$Ge = 210$</td>
</tr>
<tr>
<td>$As = 195$</td>
</tr>
<tr>
<td>$Se = 180$</td>
</tr>
<tr>
<td>$Br = 165$</td>
</tr>
<tr>
<td>$Kr = 144$</td>
</tr>
<tr>
<td>$Sn = 285$</td>
</tr>
<tr>
<td>$Sb = 250$</td>
</tr>
<tr>
<td>$Te = 235$</td>
</tr>
<tr>
<td>$I = 220$</td>
</tr>
<tr>
<td>$Xe = 228$</td>
</tr>
<tr>
<td>$U = 317.5^*$</td>
</tr>
</tbody>
</table>

Van Laar Rules

1. $C = 100$ for aliphatic and inorganic molecules
   $= 75$ for aromatic and cyclic molecules
2. $N = 85$ for $N_2$ only
3. $O = 70$ for $CO$, ethers, ketones, and alcohols
4. $H = 50$ for $H_2$ and $HCl$
   $= 34$ for all other inorganic molecules, $>NH$, $-NH_2$, $NH_3$
   $= 14$ for all other organic compounds

Note: $H = 34$ was used for $H$ attached to metallic atom.

* Interpolated values.
† Value recommended by J. C. Devins and A. H. Sharbaugh, unpublished, General Electric Co., Research Laboratory, Schenectady, N.Y.

Critical Temperature

First, use Lydersen's group-contribution technique to determine $\theta$ for the organic analogue (Table 2-1 and Eq. (2-3)). Then calculate $T_c$ (organometalllic) from Eq. (2-2), using the actual boiling point of the organometalllic.

A few comparisons of calculated and experimental critical temperatures are shown in Table H-1. The paucity of critical temperatures of complex organometalllics limits the test to simple compounds. Similarly good agreement might be expected with more complex materials since the method should have better applicability to longer hydrocarbon groups.

Critical Pressure

Simple analogue techniques similar to Riedel's method (Sec. 2-4) were found to predict $P_c$ values much larger than those found experimentally. However, from Eqs. (2-4) and (2-5),

$$P_c / P = (\omega T_c / \omega T)(\omega b)$$  \hspace{1cm} (H-1)

where subscripts $m$ and $a$ refer to the organometalllic and organic analogue, the subscript $c$ to the critical value, and $b$ is the van der Waals' constant. For the purposes of this technique, the addition method of van Laar$^*$ was used to estimate $b$ for both the organometalllic and organic analogue; $b$ contributions are given in Table H-2.

Table 11.4- (continued) Estimation of properties of organometallic compounds [11.2].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analogue</th>
<th>(\dot{P}_o), atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl₄</td>
<td>CCl₄</td>
<td>38.6</td>
</tr>
<tr>
<td>GeCl₄</td>
<td>CCl₄</td>
<td>38.3</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>CCl₄</td>
<td>38.3</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>CCl₄</td>
<td>48.2</td>
</tr>
<tr>
<td>SiCl₄F</td>
<td>CCl₄F</td>
<td>37.1</td>
</tr>
<tr>
<td>SiCl₄F₂</td>
<td>CCl₄F₂</td>
<td>34.9</td>
</tr>
<tr>
<td>SiCl₄F₄</td>
<td>CCl₄F₄</td>
<td>34.5</td>
</tr>
<tr>
<td>SiF₄</td>
<td>CF₄</td>
<td>30.1</td>
</tr>
<tr>
<td>SiH₄</td>
<td>CH₄</td>
<td>35.6</td>
</tr>
<tr>
<td>(CH₃)₃Si</td>
<td>(CH₃)₃C</td>
<td>31.3</td>
</tr>
</tbody>
</table>

\(\dot{P}_o\) (calc.) = \(\dot{P}_o\) (lit.) \times \left(\frac{\dot{T}_f \text{(calc.)}}{\dot{T}_f \text{(lit.)}} \times \frac{2b_o}{2b_o}\right).

By using Eq. (H-1), where \(\dot{T}_f\) was found by the critial-temperature procedure noted above, and with either experimental or estimated values of \(\dot{T}_f\), \(\dot{P}_o\), values of \(\dot{P}_o\) were calculated; a few results are shown in Table H-3. The agreement between experimental and calculated values is satisfactory, though not as good as for \(\dot{T}_f\).

Other Properties

If one has confidence in the estimated values of \(\dot{T}_f\) and \(\dot{P}_o\), then vapor pressures, liquid and vapor densities, thermodynamic-property variations with pressure, etc., may be determined by techniques given in this book. Kapner successfully correlated liquid density, using a method similar to the reduced method of Lutjersee et al. (Table 3-6) and vapor pressures with an Othmer plot (Fig. 4-9). This success was achieved with compounds for which no experimental critical data were available; so the use of a reduced correlation was an indirect justification of the critical-property estimation technique.

* Usually the boiling point or some reference point must be known.

11.4 Plasma Decay Profile

The Langmuir probe provides information about the electron density for a given set of experimental conditions, but it is important to model how the electron density changes throughout parameter space in order to understand when charged species directly contribute to the reaction chemistry. The profile is governed by the drift and diffusion of charged species in the gas stream, as well as loss due to recombination. The local electric field effect may be important, but it is not considered here. The terms arising from drift and diffusion can be considered similar in form to equation 11.4:
\[
\frac{dc}{dt} = v \nabla c + D_a \nabla^2 c
\]  
(11.13)

where, \(v\) is the bulk gas velocity, and \(D_a\) is the ambipolar diffusion of the particles, defined as \(D_a = D_i(1 + T_e/T_i)\), \(T_i\) is the gas particle temperature, and \(D_i\) is the gas diffusion coefficient, both are valid for weakly ionized discharges. The loss reaction is simply the contact of two charged species within a given proximity (cross-section) to one another so that they result in electrically neutral products. For these plasmas, which are by in large electropositive discharges, the reaction is \(e^- + i^+ \rightarrow n\), where \(e^-\) is an electron, \(i^+\) is an ion, and \(n\) is the neutral product. This second order reaction adds a parabolic term to the equation, \(\kappa c^2\), where \(\kappa\) is the rate coefficient. Adding this loss term to the equation yields,

\[
\frac{dc}{dt} = D_a \nabla^2 c + v \nabla c - \kappa c^2
\]  
(11.14)

At steady state, \(cd/dt = 0\) leaving,

\[
0 = D_a \nabla^2 c + v \nabla c - \kappa c^2
\]  
(11.15)

This is a second order non-linear homogeneous differential equation, therefore no analytical solutions to this equation exist, making numerical solutions the only way to map this profile.

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