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**Characterization of plasmas from a pulsed jet discharge with
applications to VUV spectroscopy and micromechanics**

Phillips, Harvey Monroe, M.S.

Rice University, 1991

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CHARACTERIZATION OF PLASMAS FROM A
PULSED JET DISCHARGE WITH APPLICATIONS TO
VUV SPECTROSCOPY AND MICROMECHANICS

by

HARVEY M. PHILLIPS

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IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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ABSTRACT

Plasmas from a pulsed jet discharge have been characterized with respect to gas species and nozzle design. Spectral lines from the gas used in the pulsed jet are apparent in the visible region. The vacuum ultraviolet spectrum, in particular for gases with high Z, is dominated by emission from species sputtered from the nozzle. Although an extensive search was made for excimer emission, no evidence of such emission was found. The production of highly ionized and excited states from materials created by the sputtering of the nozzle has possible applications in VUV spectroscopy. By operating the pulsed jet discharge at a 50 Hz repetition rate with NF_3 to produce excited fluorine ions, etch rates in excess of $10 \mu\text{m}/\text{min}$. have been achieved in silicon, which may have application to micromechanics.

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CHAPTER I

INTRODUCTION

1.1 Background and Basic Concept

Recently, a high voltage, high current discharge through a pulsed, supersonically expanding gas was reported as a potential VUV laser excitation mechanism [1]. This discharge was designed with an electrode immediately behind the orifice of a pulsed jet with a grounded wire mesh located about 1.5 cm below the nozzle orifice. Such an arrangement has achieved high peak currents (≈ 2 KA) and a very high current density (≈ 1 MA/cm²) since the discharge was confined to the small area of the nozzle orifice. This approach differed from other recent work [2-7] in that the discharge duration was short (≈ 100 ns), and currents in excess of 1 KA were employed.

Although the initial design and operation of this type of discharge with Ar as the gas species was outlined in Ref. 1, the characterization of such a device with respect to nozzle design, gas parameters, and discharge current needed further study. The first goal of this thesis, then, was to investigate the influence of these parameters as evidenced by the visible, ultraviolet, and vacuum ultraviolet (VUV) emission spectra resulting from the excitation of the gas in the pulsed nozzle as well as from the sputtered material from the nozzle itself.

1.2 Previously Reported Results

Besides the more detailed characterization of the various parameters of the system, there were several questions concerning the results and calculations reported in Ref. 1 that warranted investigation.

In Ref. 1, Stoicheff, et. al., reported laser emission from Ar_2^* . The authors attributed this emission to the lowest vibrational levels of the $^3\Sigma_u$ state of the Ar_2^* excimer which have radiative lifetimes on the order of 3 μ s. The authors reported that the linewidth of the observed transition at 126 nm was about 0.2 nm FWHM. This would correspond to a cross section for stimulated emission of approximately $3.5 \times 10^{-19} \text{ cm}^2$. Since the authors estimated the density of molecules at the location of the laser emission to be only around 10^{17} cm^{-3} , the expected gain should then have been only about $3.5 \times 10^{-2} \text{ cm}^{-1}$ instead of the reported gain of 3 cm^{-1} . If the emission came from the higher vibrational states of Ar_2^* , which have radiative lifetimes of about 150 ns, the cross section for stimulated emission would be about $7 \times 10^{-18} \text{ cm}^2$, so that a gain of about 1 cm^{-1} might have been expected. The probability, though, that such a state could have traveled from the nozzle orifice where it was reportedly produced to the point of observation 2 mm below the nozzle would have been small. With a typical thermal velocity of a particle of about 10^5 cm/sec , the excimer should have moved only about 150 μm before it decayed. In addition, the emission should have been shifted from the observed wavelength of 126 nm. If instead of originating from the triplet state, the emission came from the singlet state, a similar difficulty would have existed. The short lifetime (4 ns) would have given a large cross section for stimulated emission ($4 \times 10^{-17} \text{ cm}^2$), which could have led to a large gain, but the short lifetime would also have made the probability extremely small that the state would have survived through a transit of 2 mm.

Another difficulty with the results reported in Ref. 1 was the fact that the reported resonator design was actually a negative branch unstable resonator with a magnification (M) of -4.6. Using a simple geometric analysis, the power loss per trip ($1 - M^{-2}$) was approximately 95% [8]. Stoicheff, et. al, assumed a gain length of 3 mm, so this resonator design required that the gain be greater than 333 cm^{-1} for lasing to occur.

Thus, it was extremely difficult to understand these results, and a second goal of this thesis was to investigate the possibility of excimer emission from such a pulsed jet discharge.

1.3 Further Application for Plasma Etching

In addition to these spectroscopic studies, the ability of the pulsed jet discharge to create highly ionized species motivated an investigation into the possibility of using fluorine containing gases such as NF_3 in the discharge to etch silicon. Recent interest in micromechanics has created a need for high etch rate mechanism to produce relatively large but deep features ($\approx 10\text{-}100 \text{ }\mu\text{m}$) in contrast to applications in microelectronics, where small feature sizes ($\leq 1 \text{ }\mu\text{m}$) are required at relatively shallow depths [9]. Thus, the third goal of this thesis was to report the initial results of using a pulsed jet discharge as a high etch rate mechanism for silicon.

The content of the thesis consists of three chapters. Chapter Two will describe the construction of the pulsed jet discharge and the basic performance of the discharge. Details of the spectroscopic studies will be give in Chapter Three. Chapter Four will give the results of the studies of plasma etching. Conclusions are presented in Chapter Five.

CHAPTER II

DESCRIPTION OF THE PULSED JET DISCHARGE SYSTEM

2.1 Overview of System

A schematic of the pulsed jet discharge system is shown in Figure 2.1. A pulsed valve (General Valve) was located within the nozzle assembly and sent a short (≈ 1 ms) pulse of gas through the orifice of the nozzle into the vacuum chamber. This location for the pulsed valve had the advantage that the dead volume before the nozzle orifice was minimized. Minimizing this dead volume was important to reduce the conductance of the supersonic expansion. If the dead volume was too large, the peak pressure in the nozzle would have been lower, and a larger gas volume of gas would have escaped into the chamber before the peak pressure was achieved. Both of these factors would have degraded the supersonic expansion. The back pressure on the valve was maintained at about 3 atm. A turbopump backed by a rotary vane roughing pump restored the background pressure in the cell to a few times 10^{-5} Torr between pulses when the discharge was operated at low repetition rates (1-2 Hz). The peak pressure in the cell during a pulse measured by an ion gauge located approximately 20 cm from the nozzle was about 1 mTorr.

While the gas expanded through the nozzle, a discharge through the nozzle towards the grounded grid was initiated. The tungsten electrode was situated about 1.5 mm above the nozzle orifice, and a stainless steel wire mesh located 1.5 cm below the orifice served as the ground plane. The trigger output of the pulsed valve was used as the master clock.

Figure 2.1 Schematic of the pulsed jet discharge system and the VUV detection apparatus

In order to obtain a stable discharge, the expanding gas first had to reach the ground plane to provide a conduction path. If the discharge was initiated before the gas reach the grounded grid, the discharge would be directed up to the pulsed valve. This requirement necessitated a trigger delay of about 1 ms for the thyatron so that the discharge began about 1ms after the signal to open the pulsed value.

2.2 Description and Performance of High Voltage Discharge

A schematic of the high voltage discharge circuit is given in Figure 2.2. The maximum voltage from the power supply was 20 KV. The capacitance of the charging capacitor (C1) was 5.6 nF, and that of the peaking capacitor (C2) was 4.2 nF. With a grounded grid thyatron (EG&G HY-3202) serving as the high voltage switch, the current pulse had a FWHM of about 100 ns as measured by commercial current monitor which had a rise time of 20 ns. Some current ringing continued to about 1 μ s. At 15 KV charging

Figure 2.2 Schematic of High Voltage Circuit

voltage, the peak current was 1.8 KA. Initially, a grounded cathode thyatron (EG&G HY-32) was used as the high voltage switch. With this thyatron, however, the peak current was about half of that with the grounded grid thyatron.

Typical voltage and current waveforms are shown in Figure 2.3. The voltage was measured between the electrode and ground. The current measured was the current flowing through the electrode. Because of the finite inductance of the electrode, the voltage peaked approximately 80 ns before the current. Assuming the value of the peaking capacitor (4.2 nF) was fixed, and neglecting resistive effects, the ringing period of the current indicated that the inductance of the discharge was about 290 nH. The decay of the current ringing reveals that the resistance of the discharge reached a value of approximately 3-4 Ω . Integration of the power calculated using these waveforms gave an estimate of the energy delivered to the discharge of about 200 mJ during the initial current pulse. Since the measured current also included current from the outer charging circuit, which consisted of the storage capacitor and the thyatron, the waveform was very complicated and not sinusoidal. An indication of this was the small bump in the decay of the initial current pulse (located at a time of about 250 ns on Fig. 2.3). The timing of this bump corresponded to a peak in the current measured by a current viewing resistor located in this outer circuit. At higher charging voltages, there seemed to be significant energy dissipated during the ringing period of the discharge. From the current and voltage waveforms, it could be determined that there was a secondary peak of energy dissipation approximately 200 ns after the initial peak, with additional peaks occurring with a period of roughly 100 ns. This ringing was also observed at higher discharge voltages (> 15 KV) in the temporal behavior of the fluorescence from several spectral lines.

Figure 2.3 Discharge voltage and current waveforms

2.3 Design of the Nozzles

The nozzle assembly was designed so that the nozzle was interchangeable, and therefore, a variety of orifice diameters and nozzle materials could be studied. Discharge operation with nozzle orifices ranging from 250 to 500 μm in diameter have been characterized. With small orifices (250 μm diameter), the discharge was initially not very stable at high charging voltages (≥ 15 KV). After several hundred shots, the nozzle orifice diameter increased and the discharge became stable again. The various materials used for the nozzles included Macor (a machinable ceramic), sapphire, glass, carbon, Delrin, and PVC.

Three different nozzle designs, shown in Figure 2.4, have been used: a "standard" nozzle, an "extended" nozzle, and a "sideways" nozzle where the orifice was parallel with the optical axis. The "standard" nozzles were designed to give a supersonic expansion and to optimize the production and cooling of molecular radicals and ions [5]. Nozzle orifices made of sapphire were purchased commercially, and placed in a Macor holder similar to the "standard" nozzle. All of the "standard" nozzles made from machinable materials and the sapphire nozzles had a 45° half angle above the nozzle orifice on the high pressure side, and a 90° half angle on the vacuum side. The glass nozzles were made from glass tubing which was heated and tapered at approximately a 45° half angle until the orifice is about 500 μm in diameter. The "extended" and "sideways" nozzles were made only from Macor. The idea of the "extended" nozzle was to see the effect of prolonged confinement of the current. With the "sideways" nozzle, the objective was to study what happened within this confined region.

Figure 2.4 Cut-away view of pulsed jet nozzles: (a) "Standard" nozzle, (b) "Extended" nozzle, and (c) "Sideways" nozzle.

Calculations based on simple hydrodynamic flow of the gas through the "standard" nozzle indicated that there should have been a supersonic expansion extending far below the nozzle orifice. However, the actual situation was complicated by the presence of the grounded wire mesh, which caused scattering of the expanding gas and an increase in the ambient pressure in the region below the nozzle. In order to substantiate the existence of a supersonic expansion, photographs of the discharge were taken to confirm the presence of a Mach disk, defined as a strong shock normal to the flow direction of the gas. The existence of a Mach disk served as positive proof of a supersonic expansion. These photographs indicated that the Mach disk was located about 1 cm below the nozzle, well below the region of observation (2 mm below the nozzle). Since the gas flow upstream of the Mach disk would have been unaffected by the ambient pressure [10], the assumption of a supersonic expansion at the point of observation was verified.

Within the region of supersonic expansion, the characteristics of the gas, such as temperature and pressure, were determined by the physical parameters of the system. Given the entrance and exit orifice size and an estimate of the dead volume behind the orifice in the "standard" nozzle, the evacuation time constant of the nozzle was about 1 ms for argon. This time constant predicted that the peak pressure in the nozzle was about 2 atm assuming a 3 atm back pressure on the pulsed valve. The Mach number (M), an important characterization of a supersonic expansion defined as the particle velocity divided by the velocity of sound, can be determined for a monatomic gas by the relation:

$$M = 3.26 \left(\frac{X}{D} \right)^{\gamma-1}$$

where X is the distance from the nozzle and D is the nozzle diameter [11]. At 2 mm below the orifice, M would be around 8.2. With this value for M, the estimated pressure would be approximately 600 mTorr, the density about $2 \times 10^{17} \text{ cm}^{-3}$, and the translational temperature about 13 °K.

2.4 Detection System

Spectroscopic studies were performed with a scanning 0.2 m VUV spectrometer (Acton Research Corp.) using a photomultiplier with a scintillator as the detector with a temporal resolution of about 10 ns. The spectral range observed was 35 nm to 550 nm. The scintillator was used for both the VUV and visible portions of the spectrum. The spectral resolution of the system was approximately 5 Å. The optical axis of the spectrometer was aligned to be approximately 2 mm below the nozzle orifice, corresponding to the point of brightest VUV fluorescence. This location was determined experimentally by measuring the fluorescence of several bright VUV lines as a function of

distance from the nozzle using a movable slit with 1 mm resolution. The signal from the photomultiplier was averaged with a boxcar integrator, and the data were stored and processed in a computer. Temporal waveforms were obtained with a 400 MHz bandwidth oscilloscope.

CHAPTER III

SPECTROSCOPIC RESULTS

3.1 Spectra with Standard Nozzle Design

3.1.1 Spectral Dependence on Nozzle Material

The emission spectra from the pulsed jet discharge were studied in the wavelength range between 35 nm and 550 nm using different gas species in the pulsed jet and a variety of nozzle materials. The gases studied included *He*, *N₂*, *Ne*, *Ar*, *Kr*, *Xe*, *NF₃*, and *SF₆*. All of the spectra presented here have not been corrected for the effects of photocathode sensitivity, scintillator sensitivity, grating efficiency or window transparency. Background levels were arbitrary, having been determined by the offset of the boxcar integrator.

With "lighter" gases (gases with low *Z*, such as *He*), spectra dominated by emission from gas species in the pulsed jet were obtained. An example of a spectrum obtained with *He* using a nozzle made of Macor is shown in Figure 3.1. All of the bright emission lines could be assigned to excited helium atoms and ions. To obtain this spectrum, the gate on the boxcar was set to a width of 75 ns and was delayed 200 ns after the peak of the current pulse. This time window for observation was chosen because the spectra measured at various time delays indicated that many spectral lines were more prominent during this interval due to recombination and the effects of ringing in the discharge. More discussion on the temporal behavior of various spectra is given below.

Figure 3.1 Emission spectrum at 15 KV charging voltage, taken 200 ns after the peak of the current pulse, with *He* as the gas species and using a Macor nozzle.

When using "heavy" gases (gases of high Z , such as Ar) in the pulsed jet, however, the spectra obtained were quite different. The visible spectrum obtained with Ar while using a sapphire nozzle is shown in Figure 3.2. Although this spectrum is obviously quite complex, all the lines could be assigned to various emissions from Ar II and Ar III. The brightest lines were at 435 nm and 443 nm, which corresponded to two branches of the $3p^4(^3P)4p(^4D^0) \rightarrow 3p^44s(^4P)$ transition in Ar II. Many of the other bright lines in the region of 430-500 nm came from various multiplets of this $3p^4(^3P)4p \rightarrow 3p^44s$ transition. The lines from 350-380 nm could be identified as coming from various multiplets of the $3p^4(^3P)4d \rightarrow 3p^44p$ and $3p^4(^1D)4d' \rightarrow 3p^44p'$ transitions in Ar II. The group of lines around 330 nm apparently came from the $3p^3(^4S^0)4p(^5P) \rightarrow 3p^34s(^5S^0)$ and the $3p^3(^2D^0)4p(^3F) \rightarrow 3p^34s(^3D^0)$ transitions of Ar III [12].

The VUV spectrum, however, was dominated by lines from the sputtered nozzle material. The VUV spectrum obtained using Ar and a sapphire nozzle is shown in Figure 3.3. The time interval for observation was identical to that used for the He spectrum given in Figure 3.1. The dominant features were aluminum and oxygen lines originating from the sputtering of the sapphire (Al_2O_3) nozzle. Sputtering was due to the effective momentum transfer from the gas ions to the nozzle material. Typical ion kinetic energies inside the nozzle can be estimated to be 10 eV to several hundred eV. In this energy range, efficient sputtering of the nozzle material by heavier rare gases could be expected, whereas the sputtering efficiency of He would be low [13].

To demonstrate that these spectral features were indeed almost independent of the gas medium, a spectrum obtained with Kr in the pulsed jet discharge and a spectrum obtained using Ar are compared in Figure 3.4. Both spectra were obtained under identical conditions using the same sapphire nozzle with a 300 ns wide gate delayed 170 ns from the peak of the current pulse. The more intense spectrum using Kr was taken first, and then

Figure 3.2 Visible emission spectrum at 15 KV charging voltage, taken 200 ns after the peak of the current pulse, with Ar as the gas species and using a sapphire nozzle. Horizontal lines indicate the ranges for the transitions indicated.

Figure 3.3 VUV emission spectrum at 17.5 KV charging voltage, taken 200 ns after the peak of the current pulse, with Ar as the gas species and using a sapphire nozzle.

Figure 3.4 Comparison of emission spectra using a sapphire nozzle with *Kr* and *Ar* as the gas species. Both spectra were taken under identical conditions with a 300 ns gate delayed 170 ns from the peak of the current pulse.

the *Ar* spectrum. The intensity of the spectral features which were due to emission from the nozzle material tended to weaken the longer the nozzle was used because the orifice of the nozzle was widened by the discharge and the current density consequently lowered. Also, though somewhat dependent on the target material, the sputtering efficiency of *Kr* would in general be higher than that of *Ar* due to their mass difference. The striking similarity between the spectra and the fact that all prominent features could be assigned to emission from aluminum showed that consideration of the nozzle material was indeed crucial for the interpretation of optical spectra from intense pulsed jet discharges. Identification of these aluminum lines is given in Table 3.1. The absolute wavelengths and the differences in wavelengths corresponded within the accuracy of the spectrometer to prominent lines of *Al* II and *Al* III . Some observed lines might be combinations of two or more lines which could not be resolved. More precise identification would require a higher resolution spectrometer.

When Macor was used as the nozzle material, the VUV spectra with the "heavier" gases were dominated by *Si* and *Al* lines. These lines originated from the sputtered Macor whose complicated chemical composition includes *SiO*₂ (46%) and *Al*₂*O*₃ (16%) as the major constituents. An example with *Ar* as the gas species is shown in Figure 3.5. The time interval for observations was again identical to that of the *He* spectrum in Figure 3.1. Spectra obtained with glass nozzles showed many of the same *Si* lines. Lines identified as coming from Silicon are given in Table 3.2. As could be expected, spectra taken with carbon, PVC, or Delrin nozzles exhibited strong carbon lines.

The high degree of excitation and ionization apparent in all of the spectra was a result of initial confinement of the discharge to the small orifice allowing very high current densities ($\approx 1 \text{ MA/cm}^2$) to be achieved. Some of the spectral lines which have been

Wavelength (nm)		Species	Transition	Multiplet	f _{ik}
Observed	Tabulated				
137.9	138.27	<i>Al</i> III	4s → 3p	² S → ² P ⁰	0.129
160.7	160.57	<i>Al</i> III	3d → 3p	² D → ² P ⁰	0.937
161.2	161.19	<i>Al</i> III	3d → 3p	² D → ² P ⁰	0.843
167.2	167.0787	<i>Al</i> II	3s3p → 3s ²	¹ P ⁰ → ¹ S	1.84
172.4	172.32	<i>Al</i> II	3s(² S)3d → 3s3p	³ D → ³ P ⁰	0.901
176.5	176.4	<i>Al</i> II	3p ² → 3s3p	³ P → ³ P ⁰	0.61
185.6	185.595	<i>Al</i> II	3s4s → 3s3p	³ S → ³ P ⁰	0.129
	185.805	<i>Al</i> II	3s4s → 3s3p	³ S → ³ P ⁰	0.129
	185.472	<i>Al</i> III	3p → 3s	² P ⁰ → ² S	0.875
186.4	186.234	<i>Al</i> II	3s4s → 3s3p	³ S → ³ P ⁰	0.129
	186.278	<i>Al</i> III	3p → 3s	² P ⁰ → ² S	0.291
193.6	193.105	<i>Al</i> II	3p ² → 3s3p	¹ S → ¹ P ⁰	0.202
	193.59	<i>Al</i> III	4f → 3d	² F ⁰ → ² D	0.96
199.15	198.985	<i>Al</i> II	3s(² S)3d → 3s3p	³ D → ³ P ⁰	1.45

Table 3.1 Identification of *Al* lines seen in spectra when using gases of high Z with a sapphire nozzle. [12]

Figure 3.5 VUV emission spectrum at 15 KV charging voltage, taken 200 ns after the peak of the current pulse, with *Ar* as the gas species and using a Macor nozzle.

Wavelength (nm)		Species	Transition	Multiplet	f _{ik}
Observed	Tabulated				
110.8	111.16	<i>Si</i> III	$3s(2S)3d \rightarrow 3s3p$	$3D \rightarrow 3P^0$	0.89
112.2	112.64	<i>Si</i> IV	$3d \rightarrow 3p$	$2D \rightarrow 2P^0$	0.84
120.5	119.55	<i>Si</i> II	$3s3p^2 \rightarrow 3s^23p$	$2P \rightarrow 2P^0$	0.91
	120.651	<i>Si</i> III	$3s(2S)3p \rightarrow 3s^2$	$1P^0 \rightarrow 1S$	1.70
	120.653	<i>Si</i> III	$3s(2S)3d \rightarrow 3s3p$	$1D \rightarrow 1P^0$	1.78
	120.752	<i>Si</i> III	$3p(2P^0)3d' \rightarrow 3p^2$	$1D^0 \rightarrow 1D$	0.41
126.1	126.33	<i>Si</i> II	$3s^2(1S)3d \rightarrow 3s^23p$	$2D \rightarrow 2P^0$	1.2
129.8	129.989	<i>Si</i> III	$3p^2 \rightarrow 3s3p$	$3P \rightarrow 3P^0$	0.56
133.6	134.22	<i>Si</i> III	$3p(2P^0)3d' \rightarrow 3s(2S)3d$	$3D^0 \rightarrow 3D$	0.27
136.2	136.43	<i>Si</i> III	$3p(2P^0)3d' \rightarrow 3s(2S)3d$	$3P^0 \rightarrow 3D$	0.19
139.7	139.67	<i>Si</i> IV	$3p \rightarrow 3s$	$2P^0 \rightarrow 2S$	0.80
	141.724	<i>Si</i> III	$3p^2 \rightarrow 3s3p$	$1S \rightarrow 1P^0$	0.26
206.8	207.2	<i>Si</i> II	$3s^2(1S)4f \rightarrow 3s3p^2$	$2F^0 \rightarrow 2D$	0.09

Table 3.2 Identification of *Si* lines seen in spectra when using gases of high Z with a Macor nozzle. [12]

identified to have come from the sputtering of the nozzle material indicated the formation of states as much as 45 eV above the ground state of the neutral species. Such pulsed jet discharges could therefore have applications in spectroscopic studies of highly excited states of materials that are difficult to evaporate, or in the development of incoherent VUV light sources for other spectroscopic investigations.

In summary, consideration of the nozzle material was extremely important in interpreting the spectra obtained. If "light" rare gases, such as *He*, were used, the spectra obtained was primarily that of the gas itself. If however, "heavy" rare gases, such as *Ar* or *Kr*, were used, the VUV spectra were dominated by lines from the nozzle material. In addition, the high current density obtained in the nozzle orifice produced states as high as 45 eV above the ground state of the neutral species, which could permit the study of highly excited states of low vapor pressure materials.

3.1.2 Temporal Development of Spectra

Emission spectra from the pulsed jet discharge had a definite temporal dependence. Investigation of this temporal dependence was done by varying the time delay of the gate of the boxcar. Spectra of *He* with four different positions of the gate are shown in Figure 3.6. The gate width in each case was 75 ns. The time delay was referenced to the peak of the current pulse and included a 30 ns time delay through the photomultiplier. It was interesting to observe that in the first time period, the *He* II lines at 164 nm and 468 nm were absent, and only *He* I lines were evident. This time period began 45 ns before the current peak of the discharge, so the electron temperature was still relatively low and the observation of only neutral *He* lines would be expected. Both *He* I and *He* II lines, though, were evident in the second period, which began at the current peak, indicating that the electron temperature had increased. During the third time period, which began 150 ns

Figure 3.6 Comparison of emission spectra using He as the gas species and a sapphire nozzle taken at different delay times. The gate width in each case was 75 ns and the delay was referenced to the peak of the current pulse.
 (a) Gate started 45 ns before current peak
 (b) Gate started at current peak.

Figure 3.6 (c) Gate started 150 ns after current peak
(d) Gate started 200 ns after current peak.

after the current peak, the two ionic lines are the most prominent, with little evidence of the neutral lines. The third time period included the second peak of energy deposition caused by the ringing of the discharge. The absence of the neutral lines indicated that at the peak of the energy deposition, the gas was almost completely ionized. This fact was also collaborated by the observation that with He as the gas species, the peak current did not continue to increase with charging voltage above 15 KV. Integration of the Saha equations revealed that this condition would require an electron temperature of around 2.5 eV. The presence of both *He I* and *He II* lines in the fourth period, which began 200 ns after the current peak, indicated that recombination times must be on the order of 100 ns. Collins, et. al. have given an empirical rate coefficient for the recombination of *He II* with electrons as:

$$\alpha = \frac{8.1 \times 10^{-20} n_e}{1.0 + 0.079 P} \left[\frac{T_e}{T_a} \right]^{-4.4} \text{ cm}^3/\text{sec}$$

where n_e is the electron density, T_e is the electron temperature, T_a is the ambient temperature which is assumed to be the temperature of the ground state ions, and P is the pressure in Torr [14]. Assuming the conditions outlined above for the supersonic expansion and a fully ionized plasma, n_e would have been on the order of $2 \times 10^{17} \text{ cm}^{-3}$. With T_e taken as 2.5 eV, the recombination time constant ($1/\alpha n_e$) would have been around 175 ns, which is in good agreement with the observed rate.

VUV spectra taken with *Ar* as the gas species at four different times are shown in Figure 3.7. In this case, the gate width was set at 50 ns. Again, the time delay was referenced to the peak of the current pulse and included a 30 ns delay through the photomultiplier. Visible spectra were also taken at these various times, but showed no obvious temporal dependence, possibly because the resolution of the spectrometer was

Figure 3.7 Comparison of VUV emission spectra using a Macor nozzle and Ar as the gas species taken at different delay times. The gate width in each case was 50 ns and the delay was referenced to the peak of the current pulse.
 (a) Gate started 30 ns before peak of current pulse
 (b) Gate started 20 ns after peak of current pulse

Figure 3.7 (c) Gate started 120 ns after peak of current pulse
 (d) Gate started 170 ns after peak of current pulse

insufficient to resolve individual lines in many cases. In the VUV though, lines from higher stages of ionization could be seen to appear and disappear, indicating the rise and fall of the electron temperature. In particular, resonance lines from *Ar IV* were not present in the early stages of the discharge (time slot 1 shown in (a), which began 30 ns before the current peak), but were very bright around the peak of the discharge current (time slot 2 shown in (b), which began 20 ns after the current peak). In addition, their intensity relative to the nearby *Ar III* lines diminished somewhat in time slot 3, which began 120 ns after the current peak and is shown in (c), but increased again in time slot 4, which began 170 ns after the current peak and is shown in (d). The fourth time slot corresponded to the second major deposition of energy due to the ringing of the discharge.

Another striking feature of the VUV spectra was that the spectral lines emanating from the sputtered nozzle material tended to develop later in time, as shown in Figure 3.8. In these spectra, the gate width was 75 ns and the initial time period was centered around the peak of the discharge current while the later time period was delayed 200 ns from the current peak. The 207 nm transition of *Si II* and the resonant lines of *Al II* and/or *Al III* were weak in the initial period, but dominated the neighboring *Ar II* lines in the later time period. In many cases the temporal behavior of a spectral line was helpful in identifying its source. It should be noted that in Figure 3.8, a constant was added to the data taken at the early time period for convenience in plotting.

3.1.3 Temporal Behavior of Individual Spectral Lines

In general, the temporal behavior of individual spectral lines showed a temporal decay constant of about 100 ns, corresponding to the decay of the initial peak of the discharge current. At higher discharge voltages (> 15 KV), though, the ringing of the

Figure 3.8 Comparison of VUV emission spectra taken at different delay times at 15 KV charging voltage with a Macor nozzle using Ar as the gas species. The gate width was 75 ns. A constant was added to the data of the early gate for convenience of plotting.

(a) Gate began 30 ns before peak of current pulse

(b) Gate delayed 200 ns from the peak of the current pulse.

discharge with a period of roughly 100 ns was also seen in the fluorescence of some spectral lines.

Of particular interest was the 207 nm emission from $Si\ II\ \{3s^2(1S)4f(2F^0) \rightarrow 3s3p^2(2D)\}$ [12], which resulted from the sputtering of the nozzle material and was very bright in spectra taken with a Macor or glass nozzle using "heavy" gases in the pulsed jet. Traces of the temporal response of this line are shown in Figure 3.9. At a discharge voltage of 15 KV (a), the signal decayed after about 100 ns, corresponding to the decay of the initial peak of the discharge current. At 20 KV (b), however, the intensity became very broad in time and showed a pronounced periodic structure in its decay. When the transit time of the photomultiplier (≈ 30 ns) was taken into account, the second fluorescence peak was delayed about 200 ns from the initial current peak of the discharge. Cable delays were approximately the same for both the current transformer and the photomultiplier. The period of the later fluorescence peaks was about 80-100 ns. These features in the temporal response of the fluorescence were in good agreement with the analysis of the voltage and current waveforms.

Whereas the periodic structure in the temporal response of this line was clearly due to the ringing of the discharge, the overall broadening of the decay of this line might have also been due in part to recombination, since lines from significantly higher energy levels were also seen at higher discharge voltages. At a discharge voltage of 20 KV, the overall decay indicated a time constant on the order of 200 ns, which was longer than the decay of the discharge, and was much longer than the natural decay of the line (10 ns). There were three basic mechanisms by which this state could have been populated as indicated in Figure 3.10 [15-19]. The first would have been collisional excitation:

Figure 3.9 Traces of the temporal behavior of the intensity of the 207 nm emission of Si II at discharge voltages (a) 15 KV and (b) 20 KV.

Figure 3.10 Methods of populating the upper state of the 207 nm *Si II* emission [12, 15-17].

where $Si\ II(g)$ indicates the ground state of $Si\ II$, and $Si\ II(4f)$ indicates the upper state of interest. This mechanism would be most important when the electron temperature was low and the relative population of $Si\ II(g)$ would have been high. The next process would have been radiative recombination:

The third mechanism would have been three body collisional radiative recombination:

If the electron temperature became high enough, these later two processes would have dominated since the population of $Si\ III$ would have been much higher than that of $Si\ II$. In addition, if the electron density was high enough, collisional radiative recombination would have been dominant because of its dependence on the square of the electron density.

By comparing the species evident in the Ar spectra with the results from integration of the Saha equations for an Ar plasma, it was estimated that the electron temperature of the plasma was around 2.5 - 2.8 eV with a discharge voltage of 15 KV. The temperature was also consistent with the analysis of the recombination of He given above. Under the assumption of local thermal equilibrium, a Si plasma at these electron temperatures would have been primarily composed of $Si\ III$. In the pulsed jet discharge, the electron density would have been much greater than the density of Si and would have been independent of the relative ionization stage of Si , since the electrons came primarily from the gas species. Under these conditions, collisional radiative recombination would be expected to dominate and the time dependence of the $Si\ II(4f)$ state would be determined by:

$$\frac{d [Si\ II(4f)]}{dt} = - \frac{[Si\ II(4f)]}{\tau} + \alpha n_e^2 [Si\ III]$$

where $[Si \text{ II}(4f)]$ and $[Si \text{ III}]$ are the densities of the respective species, τ is the normal radiative decay of the $Si \text{ II}(4f)$ state, n_e is the electron density, and α is the recombination rate constant. Although a precise calculation of the rate constant for this recombination would be very difficult and beyond the scope of this thesis, the normal range for such rate constants has been shown to be a few times $10^{-28} \text{ cm}^6/\text{sec}$ for doubly ionized ions for temperatures around 2.5 eV [15, 18], but obviously would be lower when considering recombination only into one state. The temperature (T) dependence of this rate coefficient was determined to be $(250/T)^{-3.625}$, where T is here given in °K [18]. An increase in electron temperature from 2.5 eV to 3 eV, then, would have decreased α only by a factor of two. With the assumption of local thermal equilibrium $[Si \text{ III}]$ could be determined by the Saha equations to be the product of $[Si \text{ II}]$ and a function of the electron temperature T and n_e . However, since in these experiments n_e was independent of $[Si \text{ II}]$ and $[Si \text{ III}]$ this function would have only depended on T. In addition, $[Si \text{ II}(4f)]$ could be determined from $[Si \text{ II}]$ by multiplying by a Boltzman factor. Thus, the above equation for $[Si \text{ II}(4f)]$ could be written as:

$$\frac{d [Si \text{ II}(4f)]}{dt} = - \left\{ \frac{1}{\tau} - \alpha n_e^2 R(T) \right\} [Si \text{ II}(4f)]$$

where $R(T)$ is a function of temperature determined by the Saha equations and the Boltzman factor. Therefore, the term $\tau_r = 1/(\alpha n_e^2 R(T))$ could be considered as an effective recombination time constant. The radiative lifetime of this state has been given as 10 ns [12], so the value of τ_r must be on the same order to explain the observed change in the decay of the state. Since n_e was constant at around $2 \times 10^{17} \text{ cm}^{-3}$ and α was not a strong function of temperature, the value of $R(T)$ would have determined the overall effect of the recombination on the temporal decay of the state. At $T = 2.5 \text{ eV}$, the value of $R(T)$

would be on the order of 5, whereas at $T = 3$ eV this value would have been around 50. If the electron temperature increased to 3 eV with a discharge voltage of 20 KV, then the effective recombination time constant would have increased by a factor of five. Thus, it would be reasonable for recombination to have become significant at a discharge voltage of 20 KV whereas at a discharge voltage of 15 KV it was not. A factor of 5 reduction in the recombination time constant would make the change in the overall lifetime of the state unnoticeable. Taking $R(T)$ to be 50, the value for α would have to be approximately 5×10^{-29} cm⁶/sec for the overall time constant to be the observed 200 ns. With all the uncertainties of this type of calculation, this result would be considered very reasonable.

3.2 Search for Excimer Emission

Since Ref. 1 reported laser emission from Ar_2^* , much effort was made to observe and characterize Ar_2^* excimer emission around 126 nm. This spectral region was extensively explored with several nozzle materials and with each of the nozzle designs. Two alterations of the system were also tried. The first was to place a hole in the grounded grid plane below the nozzle with the hope that the supersonic expansion would be improved and the second was to place the ground plane behind the nozzle. No evidence of emission from Ar_2^* , though, was detected with any configuration. It was discovered instead that spectral lines around 126 nm were all attributable to emissions from excited species of silicon which was sputtered from the nozzle. Identification of these lines was given in Table 3.2 above.

Initially, no spectral features were observed in the region from 120-130 nm; however, when the peak current was doubled by using the EG&G HY-3202 grounded grid thyratron, spectral features began to appear. The development of these features, which

were only evident after a delay of about 220 ns from the current peak of the discharge, as a function of the charging voltage is shown in Figure 3.11. In each case the width of the gate was 75 ns and it began 200 ns after the peak of the current pulse. The similarities of these spectra revealed that no new species were created as the charging voltage was increased.

To confirm the conclusion that these spectral features indeed originated from the sputtered material of the nozzle, emission spectra around 126 nm were taken with different gases and nozzles. A comparison of the emission spectra around 126 nm taken with different gases and nozzles is shown in Figure 3.12. The gate width and time in each case were the same as for Figure 3.11. The spectra in Figure 3.12 (a) and (b) were taken with a Macor nozzle, but using *Ar* and *Kr*, respectively, as the gas species. The similarities of the spectra indicate that the spectral features did not depend on the gas, but on the nozzle material. All the lines common to the two spectra could be assigned to emission from silicon. This conclusion was further confirmed by the spectrum in Figure 3.12 (c), where *Ar* was used as the gas species but with a sapphire nozzle. The only evident feature in this spectrum was the 138.27 nm line from *Al* III (see Table 3.1).

Experiments to search for other excimer emissions, such as *He*₂^{*}, *Ne*₂^{*}, *Kr*₂^{*}, *ArF*, *KrF*, and *XeF*, were also performed, but no emission from these species in such a high current pulsed jet discharge were observed.

Molecular emission was observed with *N*₂, though, as shown in Figure 3.13. This spectrum was obtained with a gate of 300 ns beginning with the peak of current discharge. In addition to emission from the excited state of *N*₂, there was also evidence of emission from *N*₂⁺, and even some resonance lines from *N* II and *N* III, and possibly *N* IV. The creation of such highly excited states from a dissociated stable molecule indicates that, most

Figure 3.11 Comparison of emission spectra using a Macor nozzle and *Ar* as the gas species taken with different charging voltages. The gate was 75 ns and was delayed 200 ns from the peak of the current pulse. (a) 11 KV, (b) 15 KV and (c) 19 KV.

Figure 3.12 Comparison of emission spectra around 126 nm at 15 KV charging voltage, taken 200 ns after the peak of the current pulse, using different nozzles and different gases.
 (a) Macor nozzle with *Ar* as the gas species,
 (b) Macor nozzle with *Kr* as the gas species,

Figure 3.12 (c) Sapphire nozzle with *Ar* as the gas species.

Figure 3.13 VUV and visible emission spectra at 15 KV charging voltage with N_2 as the gas species using a Macor nozzle. The gate width was set at 300 ns and began at the peak of the current pulse.

likely, weakly bound molecules such as excimers were not able to survive the large electron collision rate in the high energy density region of the nozzle.

3.3 Spectra with Alternative Nozzle Designs

3.3.1 Spectra with "Extended" Nozzles

As noted in chapter two, some alternative nozzle designs were used to explore the effect of longer confinement of the high current and high pressure regions. The first attempt was to elongate the "standard" nozzle by 1.6 mm (see Figure 2.4). VUV spectra taken with this type of nozzle using *Ar* as the gas are shown in Figure 3.14. Visible spectra were also taken, but showed no appreciable change from the "standard" nozzle. The first spectrum in Figure 3.14 was taken with a 75 ns gate beginning at the peak of the discharge current. The second was also with a 75 ns gate but delayed 200 ns from the current peak. As expected from results with "standard" Macor nozzles, spectral lines from material sputtered from the Macor appeared very bright in the delayed spectrum. These spectra were very similar to spectra obtained with the "standard" nozzle taken under the same conditions; however, the delayed spectrum with the "extended" nozzle had one major new feature, a bright line at 278.8 nm. This could possibly have been the $279.8 \text{ nm } 3p(2P^0) \rightarrow 3s(2S)$ resonance transition of *Mg* II [12], but this identification was very tentative. Although *MgO* constituted 17% of Macor, this was the first spectral line from *Mg* observed.

Experiments to search for Ar_2^* emission were also conducted with the "extended" nozzle, but again no evidence of fluorescence from this species was detected.

Figure 3.14 VUV emission spectra at 15 KV charging voltage taken with Ar as the gas species and an "extended" Macor nozzle. The gate width was set at 75 ns. Horizontal lines indicate ranges for species indicated.

(a) Gate began at peak of current pulse

(b) Gate delayed 200 ns from the peak of the current pulse.

3.3.2 Spectra with "Sideways" Nozzle

In an attempt to explore what happens in the region of high current confinement, the "sideways" nozzle with exit orifices to the side, parallel with the optical axis of the spectrometer, was used (see Figure 2.4). When using this type of nozzle, the ground plane was an aluminum plate with a hole through which the nozzle was placed. A schematic of this arrangement is shown in Figure 3.15. The "flame" of the discharge would go out both orifices and up to this ground plane. A 1 mm horizontal aperture was also positioned in the exit arm of the cell, about 5 cm from the nozzle, in order to keep the signal from saturating the detector.

A spectrum taken with this nozzle configuration using *Ar* as the gas in the pulsed jet is shown in Figure 3.16. The gate for this spectrum was set at 300 ns and began at the peak of the current discharge. Interestingly, the brightest *Ar* transition in the visible region had changed. In this configuration, the brightest emission came from the $3p^44d \rightarrow 3p^44p$ transitions (351, 358 nm) whereas the brightest transitions in spectra taken under similar conditions with both the "standard" and the "extended" nozzle came from the $3p^44p \rightarrow 3p^44s$ transitions (435, 443 nm). In the long confinement region in this configuration, the electron temperature would be expected to be somewhat higher than with the "standard" nozzle. Since the 4d level is about 3.6 eV above the 4p level [12], this higher electron temperature would have made the population of the 4d level relative to the 4p level significantly higher. As before, no evidence of emission from Ar_2^* was detected.

Another change was that lines from the sputtered nozzle material were not as bright in relation to spectral lines from the gas as they were in spectra taken in other configurations. One factor was that the peak current density was reduced by a factor of two because there were two orifices. A more likely explanation, though, was that the plasma was so dense that these lines were trapped. Although exact calculation of the effect

Figure 3.15 Schematic of the pulsed jet discharge when used with "sideways" nozzle

Figure 3.16 VUV and visible emission spectra at 15 KV charging voltage taken with Ar as the gas species using an "sideways" Macor nozzle. The gate width was set at 300 ns and began at the peak of the discharge. Horizontal lines indicate ranges for species indicated.

of trapping were beyond the scope of this thesis, estimates were obtained by comparing with the calculations done by Holstein for an infinite slab and an infinite cylinder [20]. If the radiation were trapped, its decay would be described by an exponential factor of $\exp(-\gamma t)$, where γ is the Einstein coefficient for the transition and g is the "escape factor" which characterizes the escape of the radiation from the plasma. Since the pressure in the nozzle was approximately 2 atm, pressure broadening would have dominated. The g factor in this situation was computed by Holstein to be:

$$g = \frac{C}{\sqrt{\pi} k_p L}$$

where L is the characteristic dimension of the geometry, C is a constant which depends slightly on the geometry, and k_p is the center line absorption coefficient, given by:

$$k_p = \frac{\lambda_0^2 N}{2\pi} \frac{g_2}{g_1} \frac{\gamma}{\gamma_p}$$

where λ_0 is the center wavelength, N is the density of the absorbing gas species, g_1 and g_2 are degeneracy factors, and γ_p is 2π times the linewidth of the pressure broadened linewidth. For a infinite slab, L would be the distance between the slabs, and $C = 1.15$. For the infinite cylinder, L would be the radius of the cylinder and $C = 1.115$. Since the Ar pressure in the confinement region of the nozzle was approximately 2 atm, the value for γ_p can be estimated from the collision rates to be on the order of 10 GHz [21].

In order to obtain k_p , an estimate of the density of the ground state atoms was required. Experiments were done with the "standard" nozzle to measure the increase in nozzle orifice diameter as a function of the number of shots. If the assumption was made

that the sputtered nozzle material came off in atoms rather than in chunks, it was possible to estimate that approximately 1×10^{12} atoms of silicon were sputtered from the Macor for each shot. With the sideways nozzle the region of confinement was 1 mm long, approximately 100 times longer than the confinement region of the standard nozzle. The number of sputtered silicon atoms per shot, then, could have been easily been a factor of 100 higher. The corresponding density of silicon atoms in the confined region of the nozzle was then around $5 \times 10^{17} \text{ cm}^{-3}$. Integration of the Saha equation, with the consideration that the electron density in the confinement region was independent of the silicon ion density because of the much higher density of *Ar*, indicated that the density of *Si* II would have been around $3 \times 10^{17} \text{ cm}^{-3}$ at an electron temperature of 2.5 eV. Because the electron density was much higher than the density of the *Si* ions, this density was somewhat higher than what would have been expected from a pure *Si* plasma. An estimation of the density of the absorbing species, the $3p^2$ (2D) state of *Si* II, was determined to be approximately $3 \times 10^{16} \text{ cm}^{-3}$ by multiplying the total *Si* II density by a Boltzman factor.

The *g* factor calculated for the 207 nm transition in *Si* II with these assumptions and taking *L* as 0.5 mm was 1.7×10^{-2} . The effective lifetime of the state, then, was about 600 ns instead of 10 ns. Since the discharge lasted only about a hundred nanoseconds, this effective lifetime indicated that trapping was an important consideration.

In summary, emission spectra from the pulse jet discharge were studied using several gas species, three different nozzle designs, and several nozzle materials. The spectra obtained were complicated by the presence of bright spectral lines from sputtered nozzle material. Analysis of the spectra indicated that a very high degree of excitation was achieved, since states as high as 45 eV above the neutral ground state were observed. At higher discharge voltages (>15 KV), collisional recombination might have begun to

become important, as evidenced by changes in the temporal behavior of certain spectral lines. Attempts to study the high energy region within the nozzle, though, were hindered because of radiation trapping. Although an extensive search was made, no evidence of excimer emission was found with this type of discharge.

CHAPTER FOUR

PLASMA ETCHING

4.1 Motivation

Increased interest in micromechanics has created the need for faster etching mechanisms for a variety of materials. Recent work with continuous microwave discharges using a halogen containing gas has demonstrated a very high etching rate of silicon [9]. The limitation on the design of the nozzles for microwave discharges because of the need for impedance matching, though, warranted exploration of other types of discharges which are more flexible in their design parameters to see if similar etch rates could be obtained.

Other types of etching processes would not be suitable for the needs of micromechanics. Chemical wet etching would be either too slow (typically about 1 $\mu\text{m}/\text{min}$) and/or would have problems with masking. Since the chemical etchant would also attack the mask, it would be difficult to maintain the mask until the desired depth was reached. In addition, undercutting of the material under the mask would be a problem [22]. Similar problems have persisted for other dry etching processes. Typical etch rates have often been slower (0.1 $\mu\text{m}/\text{min}$) and have rarely exceeded 10 $\mu\text{m}/\text{min}$ [9]. Some type of reactive ion etching mechanism utilizing a discharge, then, would seem to be the best solution to these problems.

The ability of the pulsed jet discharge to create highly ionized species motivated the study of its feasibility as a high etch rate mechanism. When used in conjunction with a halogen containing gas, the halogen ions would etch the target material, just as in the microwave discharge. In this case, though, the nozzle design could be optimized for etching rate, since the shape of the nozzle would not greatly affect the performance of the discharge. The goal of this portion of the thesis, therefore, was to make an initial investigation to see if etch rates similar to those obtained with the microwave discharge could be obtained.

4.2 Configuration for Plasma Etching

Figure 4.1 shows a schematic of the configuration used for etching. A stainless steel wire mesh was used as test mask. The wire mesh was laid on top of the silicon wafer and mechanically held in place. The distance between the nozzle and the wafer was varied from about 1 mm to 2 mm, depending on the nozzle design. Since the etching rate fell off rapidly with this distance, the nozzle was placed as close as physically possible to the wafer. The discharge voltage was varied from 8 KV to 15 KV.

Initially, an "extended" Macor nozzle was used so that the plasma would be confined better in the desired region for etching. Sputtering of the Macor onto the wafer, however, made this configuration unacceptable. In an attempt to correct this problem, the nozzle was reconfigured to use a sapphire nozzle orifice. Because of physical constraints, though, the sapphire nozzle could be placed no lower than about 2 mm above the wafer. Nevertheless, although slightly faster etching could be obtained with the "extended" Macor nozzle, the sapphire nozzle was preferable since there was little contamination of the wafer due to sputtered nozzle material.

Figure 4.1 Schematic of the pulsed jet discharge when used for plasma etching.

After several experiments where the discharge voltage was varied, a voltage of 10 KV was chosen as a compromise between etching speed and sharpness of the etching pattern. With lower voltages, the etching rate was slower, and at a voltage of less than 8 KV, the discharge was not very stable when using NF_3 as the gas species in the pulsed jet. At higher voltages, although the etching rate was somewhat higher, the etched pattern was less clear and some melting of the wire mesh occurred.

Both NF_3 and SF_6 were used as the gas species for etching. Better results were obtained with NF_3 , most likely because the electron temperature was high enough that the dissociative attachment coefficient of NF_3 to form F^- exceeded that of SF_6 [23]. If Ar was used in the pulsed jet discharge instead of a halogen containing gas, there was no observable etching; therefore, the etching was primarily chemical and not mechanical or thermal.

4.2 Determination of Etching Rate

Two different sizes of wire mesh were used as masks. One had a spacing between the wires of about 180 μm and the other had a spacing of about 35 μm . Within the experimental error, there seemed to be no noticeable difference in the etching rate between the two different spacings, indicating that the resolution limit for this type of etching had not been reached. However, when the discharge was operated at higher repetition rates (50 Hz), the finer wire mesh tended to melt because of the heat deposited by the discharge.

Scanning electron micrographs of some etched samples confirmed that it was possible to replicate the 35 μm grid spacing over an area of about 3 mm in diameter. Optical microscopy indicated that these samples were about 50 μm deep at the deepest point. Although further optimization of the discharge parameters would be necessary to

obtain sharper features, it was encouraging that by optimizing only two parameters, the discharge voltage and the distance between the nozzle and the wafer, the wire mesh pattern could be replicated in the etched wafer.

The system was operated at 50 Hz, being limited only by heat dissipation in the nozzle assembly. Figure 4.2 shows the average of the deepest etch depth of several experiments as a function of time with the discharge system operating at 50 Hz with a voltage of 10 KV. A least squares fit indicates an etch rate of approximately 12 $\mu\text{m}/\text{min}$. With further modifications to the construction of the nozzles, so that the heat dissipation can be improved, it is anticipated the repetition rate of the discharge would be increased. The present nozzle assembly was designed to optimize the supersonic expansion through the nozzle and not specifically designed for plasma etching. Since supersonic expansion is not a requirement for plasma etching, it would be possible to improve the design so that the distance between the nozzle and the wafer could be decreased. The main difficulty was that a thin portion of Macor was too brittle to support the sapphire nozzle orifices. When the pulsed valve opened, the pressure on the sapphire orifice would crack the Macor. Solutions would be either to redesign the sapphire nozzle orifice, or to find a stronger insulating material to replace Macor. With such improvements, though, it could be possible to increase the etch rate to approximately 100 $\mu\text{m}/\text{min}$ as reported in Ref. 9.

Figure 4.2 Average over several runs of the deepest etch depth in a silicon wafer vs. the time the system was operated at 50 Hz. NF_3 was used as the gas and the charging voltage for the discharge was 10KV.

CHAPTER FIVE

CONCLUSIONS

The characterization of a pulsed jet discharge has been performed and possible applications to VUV spectroscopy and micromechanics were explored [24].

Results of VUV spectroscopic studies demonstrated that very highly excited states of *Si* and *Al* were created in the discharge. These species were produced by the sputtering of the nozzle material in the high energy region of the nozzle orifice when gases of high *Z*, such as *Ar* and *Kr*, were used. Emission from states as high as 45 eV above the neutral ground state of the species were identified. In the characterization of the discharge, it was discovered that consideration of material sputtered from the nozzle was essential in understanding the spectra obtained. The ability to create very highly excited state of atoms and ions of low vapor pressure materials such as *Al* and *Si*, though, could have applications to VUV spectroscopy.

At the highest discharge voltage (20 KV), there was some evidence that collisional recombination from higher lying states became significant. In particular, the temporal behavior of the 207 nm emission from *Si* II significantly broadened at this high voltage. Estimates of the effect of collisional radiative recombination showed that it was a feasible mechanism to explain this change.

Attempts were made to study the region of high energy density in the nozzle orifice with a special arrangement in which the nozzle orifice faced the spectrometer. Emission from the highly excited states of the nozzle material, though, was weak or not observed in spectra taken in this configuration. A possible reason was that emission was effectively trapped due to the much higher density of these species in the confinement regions and to the pressure broadening caused by the high pressure of the gas in this region.

Although extensive work was performed searching for excimer emission in this type of pulse jet discharge, no evidence for such emission was obtained. Apparently, any such molecules formed in the nozzle were destroyed by the high electron density in the nozzle orifice.

The feasibility of using a pulsed jet discharge in conjunction with a halogen containing gas as a high etch rate mechanism for silicon was also demonstrated. Etch rates of about 12 $\mu\text{m}/\text{min}$ were achieved using NF_3 as the gas species and operating the system at 50 Hz. Further improvements of the design of the nozzle assembly to allow operation at higher repetition rate should lead to increased etch rate.

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