INVESTIGATION OF DIAMOND ETCHING BY A MICROWAVE PLASMA-ASSISTED SYSTEM

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ABSTRACT

INVESTIGATION OF DIAMOND ETCHING BY A MICROWAVE PLASMA-ASSISTED SYSTEM

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Diamond deposition technology advances have opened several potential applications for diamond-based devices and components. Many diamond applications, such as micro-electromechanical systems (MEMS) fabrication and electronic devices, require the micro-structuring of the diamond and other applications, such as optical and thermal management components, require smoothing the diamond surface. Because of the high chemical inertness property of diamond, a key technique for micro-structuring and surface modification of diamond is plasmaassisted etching. The objective of this study is to investigate and develop processes and the associated understanding of plasma-assisted etching of diamond for micro-structuring and smoothing of diamond substrates.

The etching of three types of chemical vapor deposition (CVD) diamond including nanocrystalline diamond (NCD), microcrystalline diamond (MCD) and single crystal diamond (SCD) is investigated using a 2.45 GHz microwave plasma-assisted etching reactor system. The plasma reactor has a 25 cm diameter discharge located inside a 30 cm diameter cavity applicator and it has an independent rf bias capability for the substrate holder that facilitates ion energy controlled reactive ion etching at low pressures. The feed gases for the etching process include mixtures of oxygen (O_2), sulphur hexafluoride (SF₆), and argon (Ar). The etching reactor operation is investigated for both magnetized electron cyclotron resonance (ECR) and non-

magnetized plasma operation for the pressure ranges of 1-40 mTorr and 4-100 mTorr, respectively. The plasma characteristics are investigated using visual plasma discharge observations and single Langmuir probe measurements. For both ECR and non-magnetized plasma reactor operation, a high density plasma with charge particle densities of $10^{11} - 2x10^{12} cm^{-3}$ is obtained.

The etch rate, anisotropic etching profile, and surface roughness are measured versus input etching reactor parameters including pressure, substrate bias, microwave power and gas mixtures. Anisotropic etching is demonstrated and the measured etching rates range from 4 - 15 μ m/h. A highly anisotropic etching profile is obtained at a pressure of 4 mTorr. The selectivity of the plasma-assisted diamond etching process is measured for various mask materials including aluminum, gold, titanium, silicon dioxide and silicon nitride. Aluminum gave the highest selectivity with a value of 56.

The use of the plasma-assisted diamond etching process is also investigated for the smoothing or polishing of rough microcrystalline diamond (MCD) surfaces. Three plasma-assisted polishing methods investigated include the use of (1) plasma-assisted etching of MCD films coated with a sacrificial layer and etched with a selectivity of one, (2) photo-resist reflow on the rough MCD surface to expose the high portions of the MCD sample, and (3) micro-roughing of the surface by plasma-assisted etching prior to mechanical polishing. The surface roughness reduction rate and the final surface roughness obtained by the three techniques are studied and comparisons are made. The plasma-assisted smoothing of MCD samples from a surface roughness of 3800 nm down to 50 nm is demonstrated.

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CHAPTER 1

INTRODUCTION

1.1 Motivation:

Diamond has been identified as the best material for high frequency and high power electronic devices due to its excellent electrical and thermal properties [Davi, 1988]. Various types of applications were also achieved with CVD diamond including sensors [Vesc, 1996], tips for cold cathodes [Nish, 2000], electronic devices [Tsug, 2003], MEMs fabrication [Kohn, 1999], and micro-optics [Lee, 2008]. Due to advances in deposition technology, CVD diamond can now be grown over large substrate areas for nano-crystalline diamond (NCD) and micro-crystalline diamond (MCD) (150-200 mm) [King, 2008] or at high growth rates for single crystal diamond (SCD) from 50-150 μ m/h [Yan, 2002]. Those results have opened new potential applications as the prices of diamond-based devices may start to drop down.

The key problem is how to structure or smooth the diamond film due to its chemical inertness property? Etching diamond chemically (wet etch) or shaping mechanically is very hard. Most of the previous studies to fabricate structures on diamond have used the dry etching (plasma etching) method [Hwan, 2004]. Thus the etching of diamond using plasma plays an important role in post-processing of CVD diamond.

The development of diamond based devices requires an increased control over the etching process, e.g. control of the anisotropic etching, the etching rate and the surface roughness. Microwave plasma assisted etching (Electron Cyclotron Resonance (ECR) or non-Electron Cyclotron Resonance (non-ECR) is one of the suitable techniques to etch diamond because it produces high density discharges and the ion energy is controllable. The high density discharges are capable of achieving high etch rates over large substrates. The ion energy control allows minimization of the damage to the surface and achievement of anisotropic etching. This research is motivated to etch three types of CVD diamond: nano-crystalline diamond (NCD), micro-crystalline diamond (MCD) and single crystal diamond (SCD).

Besides etching microstructures in diamond, another post-deposition requirement is surface smoothing or polishing. From the nature of micro-crystalline diamond films, which have non-uniform grain sizes and randomly oriented crystal, the surface is usually rough depending on the film thickness. For selected diamond based device applications such as optical or surface acoustic wave devices, the surface roughness of the micro-crystalline diamond film needs to be low (from a few nanometers to several hundred nanometers) to reduce the thermal resistance or improve the optical transmission of diamond. The removal rate for conventional mechanical polishing is very low (eg. as low ~10 nm/hr) [Mals, 1999]. This research also is motivated to enhance the mechanical smoothing by plasma etching and shorten the time consumed for the polishing task.

1.2 Research Objective

The goal of this research project is the development and investigation of plasma-assisted etching of diamond for microstructure patterning and surface smoothing. The specific objectives to accomplish this goal include:

- Investigate the performance of a 12 inches cavity microwave plasma reactor etcher using both ECR and non ECR excitation. Characterize the plasma etcher using plasma diagnostics.
- 2. Develop and investigate diamond etching processes for high etch rate and anisotropic etching for three types of CVD diamond including nano-crystalline diamond (NCD), micro-crystalline diamond (micro-CD) and single crystal diamond (SCD). Study the effect of various plasma parameters including pressure, rf bias and gas mixtures on the etch rate and anisotropic etch profile.
- Develop diamond microstructure patterning processes using different mask materials. In particular, investigate the effect of feed gas variation in the etch gas mixture on the selectivity and etched surface roughness.
- 4. Develop and investigate methods to smooth the surface of thick and rough MCD diamond films from roughness of microns down to nanometers using plasma etching.

1.3 Outline of Dissertation

The overall research layout is described as follows. Following the brief introduction of the need of CVD diamond and the techniques to grow CVD diamond, the diamond etching methods

as found in the literature are introduced in Chapter 2. The results of diamond etching including etching rates, anisotropic etching, diamond etched surface roughness and techniques to smooth diamond surface as found in literature are discussed. Chapter 3 describes the overall structure and operation of the microwave plasma-assisted etcher used in this research. This chapter also introduces other instruments used for masking diamond and for characterization purposes. Chapter 4 discusses plasma etching theory. The plasma parameters that influence the etching will be presented in this chapter. Chapter 4 also discusses the plasma, surface reaction kinetics models and basic steps of plasma etching. A simple empirical model to calculate the diamond etch rate is also investigated. Chapter 5 will discuss the characterization of the plasma etching system. The plasma shape images are used to investigate the plasma behavior. The plasma parameters are characterized using the single Langmuir probe. Chapter 6 describes the etching results of the etcher machine. The effect of input parameters on the etch rate, anisotropic etching profile, mask selectivity and the surface roughness are presented. Chapter 7 presents the techniques to smooth the diamond surface. Finally, chapter 8 summarizes this dissertation and makes some recommendation for future research.

CHAPTER 2

LITERATURE REVIEW ON PLASMA-ASSISTED ETCHING OF DIAMOND

2.1 Introduction

This chapter reviews the methods used to etch diamond. It also discusses the results of diamond etching from the research literature. First, a brief review of diamond applications and the plasma-assisted chemical vapor deposition (CVD) is presented.

2.2. CVD Diamond Review

Diamond exhibits a unique combination of mechanical, thermal, optical and chemical properties such as high hardness, high thermal conductivity and chemical inertness. Table 2.1 shown the applications of diamond based on its superior properties.

Diamond Properties	Applications
Hardness	AFM probe, MEMS (Micro-relays, acceleration sensors).
High thermal conductivity	Heat sinks, heater for inkjet heat, flow sensors
Transparency	Windows for infrared lasers and gyrotrons, optical lenses.
Absorption of UV light	UV sensor.
Radiation hardness	Detectors for neutrons and other particles, X-ray
	lithography mask.
Large band gap	UV radiation devices for sterilization, light sources for
	UV microscopes and displays.
High electronic properties	High power, high frequency transistors, high voltage
	diodes, ion sensors, gas sensors and thermistor.
Field emission of electrons	Field emission display, field electron microscope.
Chemical electrodes	Materials sensors, bio sensors, electrochemical
	decomposition of organic materials.
Biocompatibility	DNA tip, bioreactors, micro reactors.

Table 2.1: Material properties of diamond and its future applications [Koba, 2005]

2.2.1 Crystal Structure:

Diamond is an allotrope of carbon, joining graphite and the fullerenes as a major pure carbon structure. Diamond structure as shown in Figure 2.1 consists of two face centered cubic (fcc) lattices in the primitive unit cell, one at (000) and other at (1/4 1/4 1/4). Its cubic lattice constant (a) at room temperature is 0.357 nm [Naza, 2000]. Each carbon atom has four sp³ bonds with four other carbon atoms to form a tetrahedral structure. Four valence electrons in each carbon atom form strong covalent bonds by sp³ hybridization. The atomic density of diamond is 1.77×10^{23} cm⁻³. The nearest neighbor bond length is 0.154 nm. In the cubic unit cell, there are a total of eight carbon atoms and the packing fraction is 34%.

Packing fraction =
$$\frac{8x\frac{4}{3}\pi r^3}{a^3} = \frac{8x\frac{4}{3}\pi \left(\frac{\sqrt{3}}{8}a\right)^3}{a^3} = \frac{\sqrt{3}x\pi}{16} = 34\%.$$

Because diamond has the shortest bond length of any three dimensional crystal and a high bond energy of 711 kJ/mol, it is the hardest material compared with the others [Behr, 2005]. Diamond has no infrared (IR) absorption in the one phonon region, and only a single band is observed in the Raman spectrum at 1333 cm^{-1} .



Figure 2.1: Diamond structure [source: http://newton.ex.ac.uk]

2.2.2 CVD Diamond Deposition

CVD diamond film can be synthesized using hot filament, DC plasma, molecular beam epitaxial (MBE) and microwave plasma systems. Typical conditions to grow CVD diamond are: substrate temperature range from 700-1200 0 C, chamber pressure at 20-400 Torr and methane (CH₄) concentration in gas input from 1-5% with respect to hydrogen (H₂). Under these conditions, at least more than 95% of the deposited film is crystalline diamond. Polycrystalline diamond growth contains a high density of grain boundaries. The grain boundaries can contain non-diamond carbon. Typical growth rates for CVD diamond deposition are from 0.02 µm/hr to 150 µm/hr depend on the deposition process and the deposition system type. At the low growth rate, Watanabe *et.al* reported depositing a smooth diamond layer on a (100) surface of single crystal diamond with the surface roughness R_a of 0.04 nm using a microwave plasma ASTex

system [Wata, 1999]. The growth rate was very low at19 nm/hr. The gas ratio of CH_4/H_2 was 0.025% at pressure of 25 Torr and 750 W microwave powers. High growth rates of CVD single crystal diamond were reported from 50-150 µm/h [Yan, 2002]. CVD diamond film can grow on different substrate materials such as Si, SiC, W, Mo, Cu, Pt, Ni, Ir and Pd. Besides methane (CH₄), other hydrocarbon gases such as acetylene (C₂H₂), ethylene (C₂H₄) or carbon dioxide (CO₂) have also been used to grow CVD diamond.

2.3 Diamond Etching Chemistry

2.3.1 Diamond Etching Mechanism

Plasma etching is a complex process involving several elementary processes. Some of these processes include physical sputtering (ion bombardment), chemical reactions, ion- induced (enhanced) etching, trenching, and side wall passive and mask erosion. Plasma-assisted etching has two major components including chemical reactions and physical sputtering. Basically, the chemical reaction processes consist of three sequential steps: 1. Adsorption of the etching species; 2. Product formation and 3. Product desorption [Cobu, 1979]. For diamond etching in oxygen plasmas, the chemical reactions associated with the removal of carbon atoms are given in the equations below [Moga, 1978], [Koss, 1992]:

The first step is formation of reactive oxygen species in the plasma. These reactions convert relatively inert oxygen molecules into very reactive radicals.

$$e + O_2 \rightarrow O + O + e \tag{2.1}$$

$$e + O_2 \rightarrow O^{-} + O$$
 [2.2]

$$e + O_2 \rightarrow O_2^+ + e + e \qquad [2.3]$$

$$e + O_2^+ \to O + O$$
 [2.4]

The reactive oxygen radicals then react with the diamond surface to form CO and CO₂.

$$C + n O \rightarrow CO_n (n = 1 \text{ to } 2)$$
 [2.5]

CO and CO₂ are volatile products that are released from the etching surface.

The physical sputtering mechanism is dominated by the acceleration of energetic ions formed in the plasma to the substrate surface at relatively high energies of 10's to 100's eV. Due to the transfer of energy and momentum to the substrate, surface material is sputtered away. This sputter mechanism tends to yield anisotropic profiles; however, it can result in significant damage, rough surface morphology, trenching, poor selectivity, thus minimizing device performance. In contrast, chemically dominated etch mechanisms rely on the formation of reactive species in the plasma, which interact with the substrate to form volatile etch products that are desorbed from the surface. These chemical processes tend to yield isotropic profiles and low plasma-induced damage due to virtually no physical ion bombardment of the substrate surface. However, they can also lead to lateral etching and a loss of critical dimensions thereby reducing the utility of the process for device fabrication.

Alternatively, plasma etching relies on both chemical reactions and sputter desorption of the etch products formed on the surface by energetic ions generated in the plasma. The chemical and physical components of the etch mechanism are balanced to yield high resolution features with minimal damage and optimum device performance. The dominant mechanism is determined by the volatility of the reaction by-products and the energy of the ionized species. Thus, plasma etching can include four keys process: 1. Sputtering (the material is purely physically removed by energetic ions of the gas molecules); 2. Chemical etching (the material are removed by neutral radicals formed in the plasma reacting with the substrate material to produce volatile species); 3. Ion-enhanced chemical etching (energetic ions damage the etch surface, enhancing its reactivity); 4. Inhibitor controlled chemical etching (ion bombardment removes inhibitor layers from surfaces allowing chemical etching to proceed).

2.3.2 The Diamond Etching Parameters

a) Etch Rate

The etch rate depends on the abundance of chemical active species and on the intensity of ion bombardment. The overall etch rate is calculated as follow:

$$R = R_s + R_c + R_{en} + R_{in} \tag{2.6}$$

where R_s is etch rate from the sputtering; Rc is the chemical reaction etch rate; R_{en} is the ion enhanced chemical etch rate; R_{in} is the removal inhibitor layer etching rate;

Equation (1) can be expanded as follows [Maye, 1982], [Flam, 1989]:

$$\mathbf{R} = F_1 \phi_{\mathrm{S}} + F_{\mathrm{N}} \left(1 - \alpha - \beta\right) \phi_{\mathrm{N}} + F_{\mathrm{N}} \alpha \phi'_{\mathrm{N}} + F_{\mathrm{N}} \beta \phi''_{\mathrm{N}}$$

$$[2.7]$$

where F_1 is the ion flux (ion/cm²s); F_N is the flux of neutral reactive particles; φ_S is the sputtering efficiency (cm³/ion); φ_N is the chemical etch rate efficiency of neutral species (cm³/neutral); φ'_N is the chemical etch rate efficiencies of neutral species on the fraction α of the surface which has been ion bombarded; φ''_N is the chemical etch rate efficiencies of neutral species of neutral species of neutral species on the surface fraction β covered by an etch inhibitor.

b) Anisotropic etching profile

Anisotropic etching is an important parameter of the plasma etching process. Anisotropic etching is primarily accomplished by positive ions with velocity directed toward the surface. This occurs by stimulating chemisorptions (surface damage), or by increasing the product formation or desorption. Another mechanism is the formation of recombinants which prevent further etching of surfaces on which the ions are not incident. The degree of anisotropic is directly related to the directionality of the incident ions. If several collisions occur before the ions have passed the plasma sheath, the directionality may be partially lost. Since the sheath electric field is perpendicular to the substrate and the scattering of the ions (when it occurs) is

random in direction, the field and collision induced forces on the ion compete in controlling the ion kinetic energy transport directionality (ETD) [Zaro, 1984]. The ion ETD is defined as the ratio of the random ion kinetic energy to the sum of its random and directed energy. When less or no collisions occur in the sheath, the ion energy transport becomes more anisotropic (for large mean free path or low pressure regime).

Another factor that strongly influences the anisotropic etching is the relative fluxes of ions and neutral species [Cobu, 1983]. If the ratio of the neutral flux to the ion flux is very large, the result is an isotropic etching process. In contrast if the ion-enhanced etching dominates, it is an anisotropic etching process.

c) Selectivity

This etching parameter refers to the relative etch rate of the diamond film to the etch rate of mask material (Al, $SiO_2...$) under the same plasma conditions.

There are three mechanisms for achieving selectivity [Oehr, 1990]:

- 1. Selective formation of etch inhibiting layer on one of the materials. (i.e., the situation where deposition is occurring on one material, while the other is etched under the same conditions).
- 2. Non-reactivity of the mask materials in the particular plasma chemistry employed.
- 3. Selective formation of non-volatile products on etched mask material surface.

High selectivity of plasma etching is needed to produce the required pattern resolution with minimal erosion of the mask material. A high selectivity is also needed if a thin mask material is used to pattern a deep diamond etching thickness.

d) Surface smoothness:

The diamond surface during the plasma etching is exposed to energetic particles and photon bombardment. Since etch anisotropy occurs due to ion bombardment, it is inevitable that lattice damage and surface (or sidewall) disruption will be present [Pear, 1999]. Thus, diamond-etched surface smoothness is an issue for plasma etching. A micro- masking effect can also cause the roughness of diamond etched surfaces (grass-like, whisker, or spike cone) [Ando, 2002].

2.4 Diamond Etching Systems

Recently, many dry etching techniques such as reactive ion etching (RIE), inductively coupled plasma etching (ICP), reactive ion beam etching (RIBE) and electron cyclotron resonance (ECR) have been developed and used for patterning in diamond device fabrication.

2.4.1 Reactive Ion Etching (RIE)

In RIE, the substrate is placed on the powered electrode as shown in Fig. 2.2. Etching gas is introduced into the chamber continuously. Plasma is initiated by applying a strong RF (frequency of 13.56 MHz) electromagnetic field in the chamber. The oscillating electric field

ionizes the neutral gas molecules producing electrons, reactive species (radicals and ions) and photons. On each half-cycle, the electrons are electrically accelerated in the chamber. This builds up a large negative voltage on the substrate. The positive ions diffuse to the plasma edges and are accelerated across the sheath to the substrate due to the large potential drop. Additionally, reactive neutrals (radicals) can diffuse to the substrate surface. The energetic ions and neutral radicals produce the plasma etching. Thus the RIE etching is enhanced by two processes: physical sputtering and chemical reactions. The byproduct formed after the reactive ion etching is desorbed from the surface. The volatile byproduct then is exhausted from the chamber. Typical pressures are from 4-150 mTorr and plasma density is around $10^9 - 10^{10}$ cm⁻².



Figure 2.2: RIE plasma system

2.4.2 Inductive Coupling Plasma Etching (ICP)



Figure 2.3: ICP plasma system

Inductively coupled plasma (ICP) etching is another method of plasma etching. ICP plasmas are formed in a dielectric vessel encircled by an inductive coil into which rf power is applied as shown in Fig. 2.3. The RF can be fed to helical coils wound axially around a cylindrical cavity. The power is coupled into the discharge by transformer action with the plasma acting as the secondary conductor. The frequency range is typically between 1 and 100 MHz. At these frequencies transformer coupling is efficient, although a magnetic transformer core is absent. The electric field lines induced in ICP form closed loops (in planes normal to the coil axis). This reduces significantly the electron losses to the walls as compared to capacitive

coupling RF system. Due to the reduced loss of electrons, the plasma densities attained in ICP systems are much higher as compared with RIE system. At low pressures (20 mTorr and below), the plasma diffuses from the generation region and drifts to the substrate at relatively low ion energy. So it is expected to produce low damage on the etched surface with high etch rate. The ion energy can be controlled by a second RF power supply connected to the substrate holder as shown in Fig. 2.3. At a typical pressure of 1-100 mTorr, the plasma density is around $10^{11} - 10^{12}$ cm⁻².

2.4.3 Reactive Ion Beam Etching (RIBE)



Figure 2.4: RIBE plasma system

In the RIBE system shown in Fig. 2.4, samples are separated from the ion source by one or more grids which are used to accelerate ions to the surface at highly controlled energies. Ion energies are ordinarily higher (300 to 2000 eV) than those generated in RIE or ICP. The feed gases are introduced into the chamber and cracked in the ion source. The positive ions are extracted into the ion beam and then strike onto the substrate surface creating the reactive ion etching process. The advantage of this RIBE system is all input parameters can be set independently for rapid process optimization. Although etch rates may not be as fast as those reported in ICP or ECR plasmas, RIBE etch profiles are typically anisotropic. These characteristics can be very useful in MEMS fabrication and multilayer devices (Shul, 1998). Reactive ion beam etching is also more effective in ultra-precision processing of micro-mechanical parts made of diamond provided that ion beam induced graphitization can be appropriately controlled [Miya, 1996]. However, ion beam etching has certain disadvantages, including radiation damage, a low etching rate and re-deposition [Kiyo, 1997].

2.4.4 Electron Cyclotron Resonance (ECR) Plasma Etching

Electron cyclotron resonance (ECR) microwave plasmas are used for plasma etching as shown in Fig. 2.5. They are attractive mainly due to high plasma density, which can be generated by 200-1000 W microwave powers, at low pressures of 1-10 mTorr.

Generally, microwave plasma systems can be operated both with and without external magnetic fields. These systems usually use frequencies between a few hundred of MHz and several ten of GHz with the frequency 2.45 GHz being the most common.



Figure 2.5: ECR plasma system

Typical pressures are from 1-20 mTorr for ECR and from 10 mTorr up to 100 Torr for non ECR. The plasma density is around $10^{11} - 10^{12}$ cm⁻². The energy of ions hitting the substrate can be controlled with a rf bias to the substrate.

2.5 Literature review of diamond etching

Due to diamond's chemical inertness, diamond etching using plasmas has drawn the attention of researchers. The methods and results of plasma assisted diamond etching from the literature are summarized in Table 2.2.

Туре	Sample	Gas	Power	Bias	Р	Etch	Aniso	Selec	Roug	Ref.
		Mixture	(W)	(-V)	(mT)	Rates	tropic	tivity	hness	
		(sccm)				µm/h			(nm)	
RIE	MCD	Ar:O ₂	N/A	200-	65-80	3.3-	N/A	N/A	N/A	[Sand,
		20.20		300		3.6				1989]
		20.20								
ECR	MCD	Ar:O ₂ :	400	80-	1-30	12	High	N/A	N/A	[Pear,
		SF ₆		250						1992]
FCR	MCD	1.0	500	-140	<u>л</u>	69	N/A	N/A	N/A	[Chak
LCK	MCD	Ar:0 ₂ :	500	140	-	0.9	14/21	14/14	14/14	[Cliak,
		SF ₆								1995]
		6:28:2								
RIE	MCD B	Ar:O ₂ :	200	N/A	200	0.94	High	N/A	Spike	[Dors,
	_doped	SF ₆							cone	1995]

Table 2.2: Literature Review of Plasma-Assisted Diamond Etching
Table 2.2: Cont'd

Туре	Sample	Gas	Power	Bias	Р	Etch	Aniso	Selec	Ra	Ref.
		Mixture	(W)	(-V)	(mT)	Rates	tropic	tivity	(nm)	
		(sccm)				µm/n				
RIE	MCD B	Ar:O ₂	75	50-	100	0.3-	N/A	N/A	N/A	[Vesc,
	-doped			250		1.5				1996]
		25:50								
RIE	MCD	Pure O ₂	50-350		50-	1.7-	N/A	N/A	150	[Siri,
					250	5.1				19971
		10-40								
RIE	SCD	O ₂ : CF ₄	1000	N/A	100	1.25	High	N/A	100-	[Nish,
									1000	2001]
		25%								
ECR	SCD B	Pure O ₂	1000	30-	2.3	2.4-	N/A	N/A	290	[Bern,
	-doped			140		7.2				2002]
		32								
RIE	MCD	02: CF4	300		15-	1.3-	High	N/A	0.4	[Ando,
					300	9.5				2002]
ECR	SCD	O ₂ = 55	1000	100-	2.3	3.6-	High	N/A	~12%	[Bern,
				150		7.2				2004]

Table 2.2: Cont'd

Туре	Sample	Gas	Power	Bias	Р	Etch	Aniso	Selec	Roug	Ref.
		Mixture	(W)	(-V)	(mT)	Rates	tropic	tivity	hness	
		(sccm)				μm/h			(nm)	
ICP	SCD	O ₂ : CF ₄	1000	100	15	20.1	High	26	~1	[Yama
		2%		(W)				SiO ₂		, 2007]
RIE	MCD	0 ₂ : SF ₆	300	-280	100	1.8	N/A	26	14	[Vive,
		22.5:2.5						SiO ₂		1995]
ECR	MCD	Air	130-	50	3750	1.4	N/A	N/A	71	[Herm
		100	500							, 1996]
DC	MCD	Pure O ₂	100	N/A	750	N/A	N/A	N/A	5	[Xian,
										2008]
ICP	SCD B	Ar:O ₂	600	100-	2.5	12	High	N/A	3	[Enlu,
	-doped	8:7		180						2005]

Sandhu [Sand, 1989] reported using an RIE system to etch microcrystalline diamond and carbon films. Most of the etching experiments were performed at pressures from 65 to 80 mTorr, gas flows of 40 to 80 sccm and bias voltages from 200 V to 300 V. The gas mixture used for diamond etching was argon and oxygen. The results show the etch rate increased rapidly when increasing the oxygen to argon ratio in the gas mixture up to 560 angstrom per minute (3.36 μ m/hr) and it saturated at 35 percent oxygen in the gas mixture.

Pearton *et.al* [Pear, 1992] reported a high diamond etching rate of 12 μ m/hr by an electron cyclotron resonance (ECR) microwave plasma-assisted 2.45 GHz system (Wavemat 300). The diamond etching was performed in an oxygen and argon discharge at pressures from 1 to 30 mTorr and microwave powers of 200-700 W. The substrate biases of -80 to -250 V were induced by 13.56 MHz RF power. The etch rates increased with either pressure or microwave power. The etch rate increased for biases below -100 V and then showed some saturation when the bias was greater than -100 V. It became saturated when the biases reached -250 V. The diamond etching rates also increased about 25% with the addition of SF₆ from 10-20%. A highly anisotropic etch profile was obtained at the pressure regime of 1 mTorr.

Charkraborty et al. [Char, 1995] reported a uniform etch rate up to 6.9 μ m/hr on 100 mm diameter free standing diamond wafers by an ECR microwave plasma-assisted 2.45 GHz system. The diamond etching was performed in a pressure of 4 mTorr, a microwave power of 500 W, a bias substrate of -140 V and a gas flow rate of $Ar: O_2: SF_6 = 6:28:2$ sccm.

Research on etching boron doped and undoped polycrystalline diamond was also carried out by Dorsch [Dors, 1995] using a RIE system. This study observed the formation of the columnar structures on the etched surface. In particular, four different gas mixtures were studied. In the first case, oxygen was the only gas used for diamond etching and in the second case the gas mixture was argon and oxygen. The third case used SF_6 only and the last case was an oxygen and SF₆ gas mixture. A rf power of 200 W, pressure of 200 mTorr and total gas flow rate of 40 sccm were kept the same for each etching process. The etching results showed that small cones/columns appeared after 60 seconds of the etch process in the cases of gas mixtures without SF₆. Once the columns were formed, the area between the columns etched faster than the columns themselves. In the case of etching with SF_6 in the gas mixture, the etched surface remained smooth. This paper also reported an increasing etch rate from 0.14 μ m/hr to 0.94 μ m/hr when adding oxygen in the gas mixture (at a flow rate ratio of SF₆: O₂=1:3). Using X-ray electron photo spectroscopy (XPS) to analyze the etched samples, the authors concluded that the cause of the columnar structure on the etched, doped or un-doped, polycrystalline diamond surface was due to a micro-masking effect of aluminum. Therefore, the fluorine ions efficiently removed the micro-mask to prevent the formation of columnar structures on the diamond etched surface.

Vescan [Vesc, 1996] reported using a PE 2400 RIE system to etch boron doped single crystal diamond patterned with a tungsten (W) mask. The etching gas was argon and oxygen. A diamond etch rate of 25 nm per minute (1.5 μ m/hr) was achieved with -250 W bias power. There

was an increase of the surface roughness after etching of single crystal diamond sample. The authors explained this effect due to the defects or inhomogeneous impurity distribution in the diamond leading to a strong variation of the local etch rate.

Sirineni [Siri, 1997] reported etching polycrystalline diamond films using a pure oxygen plasma with a reactive ion etching system operating at 13.56 MHz. The etching process was performed at pressures ranging from 50 to 250 mTorr and a power of 50-350 W. Oxygen flow rates were varied from 10 to 40 sccm. For polycrystalline diamond at a pressure of 200 mTorr, the etch rate was 43 nm/ min (2.56 µm/hr) and it increased up to 85 nm/min (5.1 µm/hr) at a pressure of 250 mTorr. When the input power was increased from 50 to 200 W, the etch rate also increased from 28.5 nm/min (1.7 µm/hr) to 71 nm/min (4.26 µm/hr). Generally the SEM images show that there was minimal change in the surface morphology except for the grain boundaries. When the power was increased to 250 W, uniform pitting and the appearance of columnar structures on the surface of individual crystallites was observed. The etched surface morphology also was investigated. By using the profilometer Dektak measurement, the average surface roughness (R_a) was reduced from 285 nm (original surface roughness) to 135 nm after etching. This interesting result was applied for polycrystalline diamond polishing. By doing lapping/polishing experiments, the etched diamond samples were polished at higher rates than the un-etched samples. The authors observed a darkening of the film appeared after 3, 5 and 20 min of etching polycrystalline diamond films using oxygen plasma. The darkening of the etched diamond film was explained due to scattering of light by micro-channels, fine micro-pits and /or columnar features on the surface. The authors concluded that the darkening of the etched samples was not due to graphitization of the diamond surface by RIE etching.



Figure 2.6: SEM image the anisotropic etching of single crystal diamond [Nish, 2001].

Nishibayashi [Nish, 2001] reported etching single crystal diamond by a RIE system using CF_4/O_2 (ratio of 25%) plasma. It was observed that a column on a diamond substrate has a side wall, whose top view shape is a circle with a frill, as shown in Fig. 2.6.

This study also investigated the microwave plasma etching of diamond using a CO_2/H_2 (0.5%) gas mixture at a pressure of 100 mTorr. By comparison, the SEM images show that the surface roughness after microwave etching is smoother than after RIE etching. This research also showed a new technique to fabricate sharp array tips as shown in Fig 2.7. A two steps method was used to form the sharp tips. First, RIE etching was done to form a fine column and then microwave plasma etching was used to form the sharp tip shape. In Fig. 2.6, it can be seen that the surface has many etch pits. The size and depth of the etch pits depend on both the CO_2

concentration and the etching time. The etch pits on the diamond surface can be controlled by using the gas mixture of CO_2/H_2 at 5% and 60 minute etching time. The author also concluded that the optimum conditions for anisotropic etching are the gas mixture of CO_2/H_2 at 0.5% and 1-4 hours etching time.



Figure 2.7: SEM image of the single crystal diamond emitter tips array [Nish, 2001].

Bernard *et al* [Bern, 2002] investigated the etching of p and n-type doped monocrystalline diamond using an ECR microwave plasma-assisted 2.45 GHz system. The etching rates for both n-type or p-type doped diamond were $3.6 - 7.2 \mu$ m/hr. The etching process used was a pure oxygen gas flow rate of 32 sccm and a pressure of 2.3 mTorr. The 13.56 MHz RF bias power was used to induce a DC substrate bias of -30 to -140 V. The mask material used was aluminum with a thickness of 550 nm deposited by DC sputtering. The etching rate of the n-type doped diamond slightly decreased with the DC bias from 3.6 µm/hr at -30 V to 2.4 µm/hr at -140 V. In contrast, the p-type boron doped etching rate increased from 3.6 µm/hr at -30 V to 7.2 µm/hr at -90 V. The author also reported that the surface roughness was increased with bias more than -60 V. One of the studies that related the etching rate and surface roughness is from Ando *et.al* [Ando, 2002]. A reactive ion etching Anelva L-201D-L system with 300 W RF (13.56 MHz) was used to etch doped and undoped single crystal diamond at pressures from 15 to 300 mTorr. The gas mixture was CF_4/O_2 . Some of the key conclusions from the authors were:

- The etch rates increased from 1.3 to 2.5 μ m/hr when the RF power increased from 100 W to 200 W.
- The surface roughness of etched diamond decreased when the CF₄/O₂ gas mixture ratio increased up to 25% as shown in Figure 2.8. The addition of small amounts of CF₄ into the gas mixture increased the density of atomic oxygen in the plasma that increased the diamond etch rate. An average etch rate of 9.5 µm/hr was achieved.
- A lower gas pressure led to a smooth surface and more anisotropic etching. An etched surface roughness of 0.4 nm was achieved.
- Doped and undoped diamond micro-cylinders with very high aspect ratios (approx. 8 for array structures and approx. 25 for exceptional cases) were successfully fabricated using the RIE etch system.



(a) CF₄: O₂ = 0%; (b) CF₄: O₂ = 0.4%; (c) CF₄: O₂ = 1%; (d) CF₄: O₂ = 5%; (e) CF₄: O₂ = 25%

Figure 2.8: SEM images of diamond etched under different gas ratio of CF_4/O_2 [Ando, 2002].

M. Bernard [Bern, 2004] and his research group reported using an ECR oxygen plasma system to etch single crystal diamond piece of size 3 x 3 x 0.5 mm³. The diamond etching condition was a pressure of 2.3 mTorr, oxygen flow rate of 55 sccm and bias voltage from - 100 to -150 V. They found that there was many holes in the surface etched with hole diameters of 0.3-1.6 μ m (Fig. 2.9). The hole density varied from 10⁷ to $2x10^8 cm^{-2}$. They explained that these holes originated from the defects (dislocations) of the diamond. Their

investigation also found whiskers on the surface when etching diamond with an aluminum mask. The formation of micro-masks inducing whiskers was described as due to mechanical sputtering of the edge of aluminum mask.



Figure 2.9: SEM image of the diamond surface etched without mask [Bern, 2004]

Enlund [Enlu, 2005] reported anisotropic dry etching of boron-doped single crystal CVD diamond by an ICP etching system. The single crystal diamond sample was covered with an aluminum layer with a thickness of 250 nm and then patterned by e-beam lithography. All samples were etched at a pressure 2.5 mTorr, power of 600 W and the dc induced bias was varied from -100 to -180 V. The gas mixture was 7 sccm of oxygen and 8 sccm of argon. An etching rate of 12 μ m/hr was obtained. The average surface roughness of diamond after etching was 3 nm. The diamond etch was highly anisotropic as show in Fig. 2.10.



Figure 2.10: SEM image of anisotropic etching single crystal diamond [Enlu, 2005].

Yamada and his research group also explored diamond etching with the objective to get a smooth surface and high selectivity [Yama, 2007]. This research group used an ICP system (ULVAC 3001) to etch synthetic type Ib (100) diamond with a size of $3x3x0.5 \text{ mm}^3$. The gas mixture was oxygen and CF₄. The power was 1000 W and the bias power was 100 W. The pressure regime used to etch diamond was 15 mTorr. Silicon dioxide (SiO₂) was used as the mask on diamond with a thickness of 400 nm. A two step diamond etching process was used to reduce the un-intentional whisker / micro mask effects and obtain both low roughness and high selectivity. The first step of the process was carried out using oxygen plasma only. The second step was performed for a very short period of time (from 10 to 30 sec) with the addition of a small CF₄ flow rate (2%) into the gas mixture and no bias. The etched diamond surfaces of the two step etching process observed by SEM are shown in Fig. 2.11. Fig. 2.11a shows a lot of un-intentional whiskers on the surface etched by oxygen plasma. Fig. 2.11b shows the etched surface is

smoother when a small amount of CF₄ is added in gas mixture. A high selectivity etch with a selectivity of 26 and an etch rate of 20.1 μ m/hr was also obtained. With the ratio of the gas mixture CF₄/(O₂+ CF₄) at 2%, the surface roughness R_a was 1 nm by AFM microscope. The paper also shown that when the percent of gas CF₄ increased in the gas mixture (CF₄/O₂) the selectivity of SiO₂ decreased.



Figure 2.11: SEM images of diamond surfaces etched in (a) an O_2 plasma only and (b) a

 $(O_2 + CF_4)$ plasma [Yama, 2007].

2.6 Literature review of diamond smoothing

Microcrystalline diamond films with high growth rates have promise for many applications. Because the crystal size and surface roughness generally increase when the diamond films grow thicker, there are limitations on diamond film applications where factors such as surface reflection, insufficient thermal contact or inadequate electrical contact are important. There have been many reports about microcrystalline diamond smoothing techniques in recent years. Mechanical polishing is the most popular technique used to smooth diamond films. However, the polishing rate for mechanical polishing alone is often too low (10-30 nm/hr) [Mals, 1999]. Plasma-assisted etching used alone or used in combination with mechanical polishing can increase the diamond removal rate, which reduces processing time. This section reviews work in the literature that used plasma assisted etching to smooth microcrystalline diamond films.

One of the studies of diamond smoothing using plasma etching reported on the application of an oxygen and sulfur hexafluoride (SF₆) gas mixture [Vive, 1995]. The goal of this research was to reduce the surface roughness of microcrystalline diamond films (with thickness less than 10 μ m). A RIE system (007A NEXTRAL NE110 reactor) was used with a pressure of 100 mTorr, a total gas flow rate of 25 sccm (O₂:SF₆ = 22.5:2.5 sccm) and -280 V substrate bias. Under these conditions, the etch rate of diamond was 1.8 μ m/hr. A 1.5 μ m thick mask layer of SiO₂ was deposited on the microcrystalline diamond film sample (thickness of 2 μ m) prior to etching. The SiO₂ is a preferred material because its etching rate is close to that of diamond for the etching feed gas mixture. The main purpose of the SiO₂ film was to cover the

space between the protruding diamonds from the surface. The etch process removes the diamond and SiO_2 resulting in removal of the highest diamond crystal protrusions. Specially, by using the SiO_2 as a mask layer to protect the microcrystalline diamond films surface valley regions and the diamond peaks are etched away. This planarization method significantly improved the microcrystalline diamond surface roughness from root mean square (rms) of 40 nm down to of 14 nm (measure from AFM microscope) without decreasing the film thickness.

Hermanns et al [Herm, 1996] reported using an ECR air plasma to smooth CVD microcrystalline diamond films. The average roughness of microcrystalline diamond films were reduced from 800-1000 nm down to 71 nm. A thin gold layer about 30 nm thick was deposited on the diamond film. The sample was then mechanically polished to expose the protruding areas of diamond for etching. The parameters for etching were an air flow rate of 100 sccm, a pressure of 3.75 Torr, a DC substrate bias voltage of -50 V and a microwave power varied from 130 W to 500 W. The diamond etching rate was 1.4 μ m/hr. The procedure was repeated with the thin film of gold deposited again followed by mechanical polishing and plasma etch multiple times until the desired surface roughness was achieved. One of the disadvantages of this process is the polishing of diamond films cannot be done in one step. And this process cannot smooth the roughness surface lower than 50 nm.

Z. Xianfeng [Xian, 2008] reported a new technique to smooth diamond films with DC plasma-enhanced mechanical polishing. Three microcrystalline CVD diamond film samples with thickness of 200 μ m and a surface roughness of 3.09 μ m were used for the tests. One of the

samples was not etched by oxygen plasma and others were etched with different recipes for comparison purposes. Then all films were polished by a mechanical polishing device with diamond powders as the abrasive. The authors observed a significant reduction of the surface roughness with the samples processed with the pre-plasma etch. The samples with a pre plasma etch had the surface roughness R_a reduced down to 30 nm compared with 1532 nm without using the pre plasma etch treatment. The plasma etching can lead to the emergence of numerous etch whiskers on the diamond grain surface which can be removed quickly with the mechanical abrasive device. By repeating the oxygen plasma etching treatment, the surface roughness of diamond films can be polished from 3000 nm to 5 nm within 5 hrs.

2.7 Summary

Plasma-assisted diamond etching has been reviewed. Three different types of diamond, nanocrystalline, microcrystalline and single crystal materials have been etched by plasma-assisted etching systems. The ECR plasma and ICP plasma systems gave the higher etch rates as compared to RIE plasma systems. The etch rates range from 1.3 to 20 μ m/ hr. Whiskers can form on the diamond surface because of micro-masking when etched with an oxygen plasma alone. Plasma-assisted etching has also applied to smooth microcrystalline diamond surfaces.

CHAPTER 3

EXPERIMENTAL EQUIPMENT AND METHODS

3.1 Introduction

In this chapter, the experimental equipment and methods to be used in the study will be described. The first section in this chapter will focus on the structure and performance of the Lambda Technologies Etcher system. Section 3.3 will introduce other equipment and methods used to support the diamond etching research.

3.2 Microwave Plasma Assisted Etching System

This section overviews of the major components of the experimental etching system and then goes over the detail of each component. The Lambda Technologies, Inc microwave plasma assisted etching system (Fig. 3.1) consists of: (1) The Microwave Power System; (2) The Microwave Plasma Reactor; (3) The Vacuum System; (4) The Bias System; (5) The Gas Delivery System; (6) The Cooling System; (7) The Control and Computer System. Each of these components is described in detail in the sections below.



Figure 3.1: Block Diagram of the Microwave Power System. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

(1) Microwave Power System	(5) The Gas Delivery System
(2) Microwave Plasma Reactor	(6) The Cooling System
(3) The Vaccuum System	(7) The Computer
(4) The Bias System	(8) Substrate Holder

3.2.1 The Microwave Power System

An ASTeX F120163 microwave power generator provides a power up to 1800 W at a frequency of 2.45 GHz as shown in Figure 3.2. The output of the microwave power supply

magnetron is connected to the three port circulator GA1112 (2). This circulator is used with dummy loads GA1201 (4) in an isolator configuration for magnetron protection. The dummy load uses water as the absorptive medium in a polyethylene insert to provide good performance for up to 3000 W continuous input power. The other port of the circulator is connected to an impedance matching head ASTeX 0453 with precision power detector (3) to maximize the power transfer and minimize the reflection from the plasma load. The incident and reflective powers were monitored through a power detector unit (3) and output to a LabView program. The power detector (3) is connected to probe (6) through a wave guide (5).



Figure 3.2: Block Diagram of Microwave Power System

(1) 2.45 GHz power supply; (2) circulator; (3) power detector; (4) dummy load; (5) wave guide; (6) Excitation Probe

3.2.2 The Microwave Plasma Reactor

The microwave plasma reactor is the latest version of a microwave reactor with a quartz enclosed plasma disk discharge that was introduced in the early 1980's by Root and Asmussen [Root, 1985]. The microwave plasma reactor used for the etching experiment, was constructed by Lambda Technologies, Inc, based on the latest version of microwave plasma reactor as shown in Figure 3.3.

The microwave plasma reactor consists of a 30.4 cm diameter brass cavity applicator (1), sliding short (2) allowing adjustment of the length of the cavity, and excitation probe (3). The sliding short and probe can adjustable in the up and down direction. Finger stock (4) is used to provide electrical contact between the sliding short and cavity walls. The plasma discharge is generated in the volume of the 24 cm inner diameter, 15 cm tall, quartz bell jar (6). The bell jar is cooled by compressed air cooling holes (7) equally spaced around the bottom of the bell jar. The etch processing gases enter the chamber through pin holes (9) equally spaced around the stainless steel base plate (11) at the bottom of the bell jar. The ECR magnet ring (12 poles) configuration, as shown in Figure 3.4, is placed in the apparatus near the center plane of the discharge. The magnet ring is cooled by the water cooling channel (5).



Figure 3.3: Diagram of Microwave Plasma Reactor

- 1) Brass Cavity 6) Quartz Dome
- 2) Brass Sliding Short 7) Air Cooling hole
- 3) Excitation Probe 8) Magnets Location
- 4) Finger Stock 9) Gas Channel
- 5) Water cooling 10) Rubber O-Ring
- 11) Stainless Steel Base Plate



Figure 3.4: Magnets ring configuration

- North poles: Red
- South poles: Blue

3.2.3 The Vacuum System



Figure 3.5: The Vacuum System

Vacuum Chamber 7) Turbo Pump
 1000 Torr Pressure Gauge 8) High Vacuum Throttle Valve
 Medium Vacuum Throttle Valve 9) 1-10 Torr Baratron Gauge
 Isolation Valve (pneumatic) 10) 0.1-1 Torr Baratron Gauge
 Roughing Pump 11) Cold Cathode Gauge PTR90
 Foreline Gauge (3.75 10⁻⁶- 10 Torr)

The vacuum system consists of paths for medium pressures (1- 800 Torr) and high vacuum pressures (1mTorr-1 Torr) as shown in Figure 3.5. The roughing pump is a rotary vane vacuum pump (5), a model TRIVAC D 40 BCS-PFPE two stage pump which can reach a base pressure down to 8 x 10^{-4} mbar or 0.6 mTorr. Path one consists of a roughing pump (5), isolation valve (4), medium throttle valve (3) and a 1000 Torr pressure gauge (2). This path of pumping is mostly used for higher pressure regime etching processes (for non-ECR plasma processes). Path two consists of the roughing pump (5), an isolation valve (4), a foreline gauge (6), a turbo pump (7) and a high vacuum throttle valve, i.e the Intellisys throttling softshut gate valve (8). This path controls high vacuum pressures of 1 mTorr up to 1 Torr (for ECR plasma process). Three vacuum gauges (9), (10) and (11) of different pressure ranges are connected to the pressure controller to monitor the vacuum chamber pressure.

3.2.4 The Gas Delivery and Cooling System



Figure 3.6: The Gas Delivery and Cooling System.

1)	Gas Botle	6) NesLab Chiller
2)	Mass Flow Controller	7) Base Pate
3)	Affinity Chiller	8) Dummy Load
4)	Substrate Holder Stage	9) Microwave generator
5)	Bias Matching Network	10) Multi-gas controller 647 C

The gas delivery system consists of the source gas cylinders (1) (Oxygen, Nitrogen, Sulfur Hexafluoride and Argon), four mass flow controllers (2) and the multi-gas flow controller unit 647 C (10). The maximum flow for source gases (from MKS mass flow controller) are 20 sccm for oxygen (O₂) gas (channel 01); 200 sccm for argon (Ar) and nitrogen (N) (channel 3 and 4) and 10 sccm for sulfur hexafluoride (SF₆). The MKS 647 C controller (10) controls both pressure and flow of gases into the chamber both manually or through the computer. The cooling system consists of two chillers (3 and 6). The Infinity chiller (3) cools the substrate holder (4) and the matching network unit (5). The NesLab Chiller (6) cools the base plate (7), the dummy load (8) and the magnetron (9).

3.2.5 The Performance of Plasma Etcher

This section investigates the performance of the 12 inch cavity applicator which couples microwave power into the plasma. The short and probe adjustments were studied to optimize the etcher operation in the TM_{013} and TM_{012} modes. Figure 3.7 shows the microwave resonant frequency versus the cavity length L_s for an ideal cavity (diameter of 12 inches). With a microwave frequency of 2.45 GHz, the TM_{012} and TM_{013} resonant modes occur at cavity lengths of 12.8 cm and 19.2 cm, respectively.

Figures 3.8 to 3.10 show the experimental microwave absorbed power versus cavity length at pressures of 1 mTorr, 10 mTorr and 40 mTorr, respectively. The absorbed microwave

power is determined as the incident microwave power minus the reflected microwave power. For the pressure of 1 mTorr, the highest absorbed power occurs from 19 cm to 21 cm for the microwave incident power from 500 - 900 W. For the pressure of 10 mTorr, the highest absorbed power occurs from 19.5 cm to 20.1 cm for the microwave incident power from 500 - 900 W. And at the higher pressure of 40 mTorr, the highest absorbs power occurs around 20.2 cm for the microwave incident power from 500 - 900 W.



Figure 3.7: The Cavity Modes



Figure 3.8: The absorbed microwave power versus cavity length L_S (pressure of 1 mTorr)



Figure 3.9: The absorbed microwave power versus cavity length L_S (pressure of 10 mTorr)



Figure 3.10: The absorbed microwave power versus cavity length L_s (pressure of 40 mTorr)

3.3 Other Related Instruments

This section describes other instruments used for diamond etching research.

i) Clean room

Except for the Etcher, most of the instruments are housed in a class 1000 clean room located in Research Complex Engineering Building. Several essential instruments used for this research include a wet station, a Suss MJB3 mask aligner, a photoresist spinner, an Axxis Physical Vapor Deposition (PVD) system, and a Plasma Enhanced Chemical Vapour Deposition (PECVD) Plasmalab 80 Plus system. Details of selected equipment in the clean room include:

ii) The PECVD system

The PECVD Plasmalab 80 Plus, made by Oxford Instruments Plasma Technology, can be used for deposition of silicon oxide, silicon nitride and amorphous silicon. This instrument is a 13.56 MHz driven parallel plate reactor with manual sample loading and heated substrate. This machine is controlled by a PC that runs the PlasmaLab 800 software. The 10 inch substrate holder is capable of heating up to 700 C degree. The deposition rates for silicon oxide and silicon nitride are approximately 3 μ m/hr and 1.2 μ m/hr, respectively. This machine is used to deposit the silicon oxide or silicon nitride films used as masks on diamond samples.

iii) The PVD system

The PVD deposition (Axxis_Lesker) provides three mechanisms for thin film deposition: thermal evaporation, electron beam evaporation, and magnetron sputtering (RF or DC). This machine is capable of depositing a variety of conductive or insulating multilayer thin films. The substrate holder can hold up to 6 inch diameter substrates with rotation and heating. The vacuum chamber pressure can reach to 5 x 10^{-7} Torr. The typical film uniformity is better than +/- 5%. This machine is used to deposit thin films (Al, Gold, and Ti) as masks on diamond samples.

iv) Mask Aligner

The mask aligner, model Karl Suss MJB3, is used for patterning photoresist through a photolithography mask. The exposure source is a 350 W Hg lamp powered by a Suss model 505 supply. The system incorporates UV-400 optics to transfer the energy to the substrate. The UV light source can operate either in constant power or illumination mode. The process diamond sample is mounted in the chuck and held tightly by the vacuum. This machine is used to transfer the pattern using a mask for selectivity, diamond etching and anisotropic studies.

v) Photoresist Spinner

The spinner, model WS-400 manufactured by Laurell Technology Inc, is used for coating photoresist on the top of diamond substrates/films. The spinner chamber is made of polypropylene (NPP), which is imperviously to chemical attack. The spinner can rotate up to 8000 rpm. For this research, the spinning speed was at 3000 rpm for 30 sec.

vi) Dektak Profilometer

The Dektak profilometer (model D6M) is used for measuring the thickness and surface roughness of diamond surface samples. The profilometer traces the surface of the sample with a floating diamond needle that records the z axis fluctuations (using the low-inertia sensor head). This equipment is used to determine the etch rate, surface roughness and selectivity.

vii) The Optical Microscope

An optical microscope (model Nikon ME600) is used to observe and take micrographs of the diamond etched surface in order to characterize the surface morphology. Magnifications of 100 X and 500 X are mostly used for this research project to observe the surface morphology.

viii) SEM Microscope

Scanning Electron Microscopes (SEM) (model JOEL 6400V and 7500F), located in the Center of Advanced Microscopy, are used to characterize the surface morphology of etched diamond. SEMs operate by scanning a focused electron beam over a surface and sensing the secondary electrons emitted from the surface. SEMs have high magnification in the range of 50-40000 X (JOEL 6400V) or even up to 500000 X (JOEL 7500F). The microscopes are helpful to measure the step height of etched profiles.

CHAPTER 4

PLASMA ETCHING THEORY

4.1 Introduction

Plasma etching is the most common method used to etch diamond because diamond is chemical inert for all liquid etching acids and solutions. Plasma etching relates to many complicated processes that need to be broadly understood. There are reviews and discussions about plasma etching and processing in the research literature [Chap, 1980], [Lieb, 1994] and [Shul, 2000]. This chapter overviews plasma etching, especially in regards to plasma-assisted etching of diamond.

4.2 Plasma Etching Fundamentals

Plasma is an ionized gas with free positive and negative charges in equal number, neutral atoms, radicals or molecules, in addition to photons emitted from excited species. Radicals are molecule fragments with unsaturated bonds. Positive charge carriers are mostly ionized atoms, radicals, or molecules created by impact with electrons. And negative charges are free electrons and some negatively charged ions. Neutral atoms, radicals and molecules can be in the ground or excited state. When excited species lose energy via spontaneous transitions to lower energy states, photons are emitted. The most important form of energetic particle bombardment on surfaces in plasma assisted etching system is positive ions. Negative ions and electrons are much less important than positive ions because they have very little energy when they reach surfaces.

Plasmas can be created by applying a sufficiently large electric field to a gas. The electrons which gain kinetic energy from the applied electric field then collide with and transfer energy to gas atoms. It results in ionization and excitation of gas molecules/atoms. The charged particles can be neutralized by recombination within plasma or at the chamber wall. The plasma is maintained when the rate of ionization of gas atoms or molecules is equal with the rate of electron and ion recombination [Maha, 99].

4.2.1 Plasma parameters

The simplest view of a plasma-assisted etching discharge is electrical energy is coupled to the electron gas, which excites the electron gas. The electrons through collisions drive ionization reactions that produce a plasma discharge that has a similar number of positive and negative particles. At the boundaries of the discharge, where the plasma discharge interacts with the walls, a plasma sheath is formed. Since the electrons are more energetic and mobile in the discharge than the positive ions, a potential is established between the quasi-neutral plasma and the wall that helps repel electrons from the wall and attracts positive ions to the wall. The potential of the quasi-neutral discharge region away from the wall is called the plasma potential V_p . An important quantity to help understand the size of the plasma sheath is the quantity called the Debye length λ_D . The Debye length is a measure of the distance that a single charge in the plasma has an influence on the local potential variation. Assuming that the electrons are a collection of independent particles obeying Maxwell-Boltzmann statistic, the electron density $n_e(\mathbf{r})$ will be distributed in the potential φ as follow:

$$\frac{n_e(r)}{n_{e0}} = \exp\left\{\frac{e\Phi(r)}{k_B T_e}\right\}$$
[4.1]

where: k_B is the Boltzmann's constant =1.38 10⁻²³ JK⁻¹; T_e is the electron temperature; n_{e0} is the average electron density; $\varphi(r)$ is the potential around a charge q can be computed as follow

$$\Phi(r) = \left(\frac{q}{4\pi\epsilon_0 r}\right) \exp(-r/\lambda_D)$$
[4.2]

where ε_0 is the permittivity of free space $\varepsilon_0 = 8.854 \ 10^{-12} \text{ F.m}^{-1}$ and λ_D is the Debye length (the scale length over which a plasma can be considered neutral).

At a pressure of 4 mTorr, the Debye length in typical high density plasma that may be used for plasma assisted etching is approximately [Suga, 1998]:

$$\lambda_D = \left(\frac{\varepsilon_0 k_B T_e}{n_e e^2}\right)^{1/2} = \left(\frac{8.854 \times 10^{12} \times 1.38 \times 10^{-23} \times 5}{8.5 \times 10^{17} \times 1.6 \times 10^{-19}}\right)^{1/2} \approx 2.1 \times 10^{-5} m$$
[4.3]

Microwave is one of the plasma sources which can be used to generate high density plasmas. The microwaves (2.45 GHz) created by a magnetron, are introduced into the discharge chamber via a transmission line or waveguide. The electromagnetic waves are propagated into the working gas region (confined by the quartz discharge chamber) where the plasma is excited.
In low pressure microwave etching reactors the coupling of microwave energy into the electron gas normally occurs by joule or collision heating and also by electron cyclotron resonance heating in a magnetized system.

The average energy gain of an electron from the microwave energy in unit time due to Joule and ECR heating is given by the following equation [Asmu, 1989]:

$$W = \frac{e^2 E^2 v}{4m_e} \left[\frac{1}{v^2 + (\omega - \omega_c)^2} + \frac{1}{v^2 + (\omega + \omega_c)^2} \right]$$
[4.4]

where ω is the microwave operating frequency; E is the microwave electric field; v is the collision frequency between electrons and gas molecules and ω_c is the electron cyclotron resonance frequency in a static magnetic field as given by:

$$\omega_c = \frac{eB}{m_e} \tag{4.5}$$

where m_e is the mass of the electron; and e is the charge of the electron, and B is the strength of the static magnetic field.

Under low pressure conditions (<< 100 mTorr) and with the presence of the magnetic field, the mean free path of electron-neutral and electron-ion collision becomes very long, then $\nu \sim 0$. If $\omega = \omega_c$ then W $\rightarrow \infty$. This is called electron cyclotron resonance (ECR). At higher

pressure, the energy absorption becomes collisional and the magnetic field has a little or none influence on the heating of the electron gas. ECR plasma (2.45 GHz) is not useful when it operates in a high pressure regime (p > a few 10 mTorr).

In the case of non-magnetized, then $\omega_c = 0$. Equation [4] becomes:

$$W = \frac{e^2 E^2 v}{2m_e} \left[\frac{1}{v^2 + \omega^2} \right]$$
 [4.6]

In this case the heating is called Joule or collision heating. The energy absorption becomes a maximum when $\omega = v$. The electrons are accelerated by the alternating electric field of the microwave. The energy absorption W depends on the collision frequency. From equation (6), it is clearly see that at very low pressure, the collisional frequency is much lower than the operating frequency, and then the energy absorption becomes less. So the discharge is harder to maintain.

4.2.2 Theory of microwave propagation

In theory, microwaves cannot propagate in plasmas with densities higher than a maximum plasma density N_{cr} which is determined by the following equation (B = 0) [Popo, 1991]:

$$N_{cr} = \frac{\omega^2 m}{4\pi e^2}$$
[4.7]

where m is electron mass and e is electron charge and ω is the microwave angular frequency.

With the present of magnetic field, the wave propagation is reflected by a cut off plasma density N_{cutoff} is determined as follow:

• For $B > B_{Ce} = 875 G$.

$$N_{cutoff} = N_{cr} \left(1 + \frac{B}{B_{ce}}\right)$$

• For $B < B_{Ce} = 875 \text{ G}.$

$$N_{cutoff} = N_{Cr} \left(1 - \frac{B}{B_{ce}}\right)$$

The plasma skin depth, the depth which electromagnetic waves can penetrate into plasma, is calculated as follow [Huba, 2007]:

$$\delta = \left(\frac{m_e}{e^2 \mu_0 n_e}\right)^{\frac{1}{2}} = 5.31 \times 10^5 n_e^{-\frac{1}{2}} \,(\text{cm})$$
[4.8]

where μ_0 is permeability (free space); n_e is the electron density; m_e is the mass of electron and e is the electron charge.

For 4 mTorr pressure regime and an assumed the electron density (Ar=10 sccm) of ~8.5 x $10^{11} cm^{-3}$, using the Equ. 4.8, the plasma skin depth is approximately 4.89 cm. Given the size of the discharge region in the microwave etching used in this study, it can be concluded the microwave energy a penetrate substantially into the discharge with size of ~10-25 cm.

4.2.3 Plasma-wall interaction

Plasma consists of electrons and ions. The electrons, with smaller mass, move more rapidly than ions because of higher thermal velocity [Mass, 1979]. So the electrons are the first species to reach any surface that is exposed to the plasma. This results in the electric potential at the surface (wall) becoming lower than the plasma potential. Electrons are repelled from the surface and the positively charged ions are attracted to the surface. The corresponding decrease of the electron density is presumed to form a positive space charge region shielding the plasma from the negative wall and this is called the sheath. Thus the sheath is a finite region over which the potential drops from the plasma potential V_p to the potential at the surface. Figure 4.1 and 4.2 show a schematic of the sheath potential in front of a wall [Schn, 2001] [Stev, 2000].



Figure 4.1: Schematic of the plasma sheath region in front of the wall [Schn, 2001].

Generally, there are three regions in the plasma regime: the sheath, pre-sheath and bulk plasma as shown in Fig.4.2.



Figure 4.2: Plasma density and potential across a sheath [Stev, 2000]. The relevant plasma parameters are shown: ion density in the sheath region n_i , electron density n_e , ion density in the bulk plasma n_{i0} , plasma potential V(x), sheath edge position d and the pre-sheath edge position L.

A sheath region ($x \le d$) is the region where the electron density drops well below the ion density. A pre-sheath region ($d < x \le L$) is a quasi-neutral transition region between the sheath and the bulk plasma (x>L).

The plasma sheath is the interface between the bulk plasma and the chamber wall or the substrate material. Sheaths are particularly important because their properties determine how the ions from the plasma interact or sputter onto the substrate surface [Stev, 2000]. The thickness of the plasma sheath is given as follow [Suga, 1998]:

$$d = \frac{\lambda_D}{0.98} \left(\frac{e(V_p - V_f)}{k_B T_e} - 1 \right)^{3/4}$$
[4.9]

where k_B is the Boltzmann constant, ϵ_0 is the permittivity of the vacuum, V_p is the plasma potential and λ_D is the Debye length (see Equ. 4.3).

At a pressure of 4 mTorr, the sheath thickness is approximately:

$$d = \frac{\lambda_D}{0.98} \left(\frac{eV_p}{k_B T_e} - 1 \right)^{3/4} = \frac{2.1 \times 10^{-5}}{0.98} \left(\frac{28 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 5 \times 11605} - 1 \right)^{3/4} \approx 6.7 \times 10^{-5} (m)$$

Hence, the sheath thickness is usually a few Debye lengths in size.

4.2.4 Ion kinetic energy

When a flux of ions which are accelerated in the sheath is incident on a surface, they initially transfer momentum to target atoms. The incident ion can both (1) lose momentum in subsequent collisions, and finally come to rest in thermal equilibrium with the target (implantation) or (2) get reflected from the target (backscattering).

The maximum ions energy that strikes on an electrically isolated substrate depends on the difference between the plasma potential V_P and the floating potential V_f . The voltage drop across the sheath is given as follow [Chap, 1980]:

$$\mathbf{V}_{\mathbf{S}} = \mathbf{V}_{\mathbf{p}} - \mathbf{V}_{\mathbf{f}} = \frac{k_B T_e}{2e} \ln \left(\frac{m_i}{2.3m_e} \right)$$

$$[4.10]$$

where e is the charge of electron; k_B is the Boltzman's constant; m_i and m_e is mass of the ions and electron respectively; T_e is the electron temperature.



Figure 4.3: Diagram of etcher plasma with RF biasing

The collision of ions in the sheath region can also decrease the ion energy incident on the surface. The energy of positive ions striking the substrate can be increased by applying a

negative bias onto the substrate. Most plasma etching processes require a bias potential with a negative bias applied to the substrate to ensure directional ion bombardment or anisotropic etching. When a RF power is applied to the substrate as shown in Fig. 4.3, the voltage dropped across the plasma sheath will be increased without increasing the ion current drawn to the substrate [Caug, 1991]. So the ion energy is controlled independently from the current density. The ion is accelerated by the electric field in the sheath, strikes on the surface and promotes the etching process. The voltage sheath drop across the sheath is expressed as follow [Mant, 1983]:

$$V_{dc} = -\frac{k_B T_e}{2e} \ln\left(\frac{2m_i}{\pi m_e}\right) - \frac{k_B T_e}{e} \ln\left(I_0 \left[\frac{e^2 V_{rf}}{k_B T_e}\right]\right)$$

$$[4.11]$$

where V_{dc} is the negative dc substrate voltage; I_0 is the modified Bessel function; V_{rf} is the external alternating voltage peak bias source.

When
$$V_{rf} \rightarrow 0$$
 (no bias), then $V_{dc} \rightarrow V_f = \frac{k_B T_e}{2e} \ln\left(\frac{2m_i}{\pi m_e}\right)$ [4.12]

When
$$V_{\text{rf}} \ge 10(\frac{k_B T_e}{e})$$
, $\ln\left(I_0\left[\frac{e^2 V_{rf}}{k_B T_e}\right]\right) \approx 2\frac{eV_{rf}}{k_B T_e} - \ln\left(2\pi\left[\frac{e^2 V_{rf}}{k_B T_e}\right]^{1/2}\right)$ [4.13]

And;

$$V_{dc} \approx -V_{\rm f} - 2V_{\rm rf} + \frac{k_B T_e}{e} \ln \left(2\pi \left[\frac{e 2V_{rf}}{k_B T_e} \right]^{1/2} \right)$$

$$\tag{4.14}$$

Thus for the large peak applied bias voltage ($V_{rf} \ge 10 \quad \frac{k_B T_e}{e}$), the negative DC substrate

bias equals the floating potential plus the peak to peak applied voltage minus a positive

correction term
$$\left(=\frac{k_B T_e}{e} \ln \left(2\pi \left[\frac{e^{2V_{rf}}}{k_B T_e}\right]^{1/2}\right)\right)$$
. This correction term is relatively small compared

with the peak voltage V_{rf} . Therefore, the voltage V_{dc} is slightly less than the peak voltage V_{rf} and proportional to it. Equation [14] showed good agreement with experiment data for $eV_{rf}/(k_BT_e)$ from 0 to 150 as shown in Figure 4.4.



Figure 4.4: V_{dc} versus V_{rf} peak in argon plasma, pressure = 1mTorr, T_e =1.8 eV and V_f =-7.9 V [Mant, 1983].

At low pressures, it can be assured the ions have no collisions in crossing the sheath. Ions that fall through a plasma sheath potential are accelerated normal to the substrate by V_{dc} sheath

potential with an energy of
$$\varepsilon_{i} \approx -e(V_{f} + V_{rf} - \frac{k_{B}T_{e}}{e} \ln \left(2\pi \left[\frac{e2V_{rf}}{k_{B}T_{e}}\right]^{1/2}\right)$$
). So a larger negative

bias will give more energy to the ions striking on the surface to be etched. This result in vertical etches rates being large as compare to lateral etch rates. That means the anisotropic degree and the etch rate are affected by the negative bias applied to the substrate. By contrast, lower negative bias voltages decrease the anisotropy and etching rates.

4.2.5 Plasma Density

Plasma density is an important parameter to determine the reaction rates in the plasma. The ions, electrons and neutrals vary by mass, temperature and power absorbed. The electron density is approximately equal to the ion density locally, but they are both typically less than the density of neutrals. In the case of a low pressure, non-magnetized chamber, the random motion of the ions and electrons to the substrate takes place equally by am bipolar diffusion. The plasma density becomes almost uniform over the entire discharge except adjacent to the wall. The plasma density can be determined experimentally using a Single Langmuir Probe (SLP) as follow:

$$n_i = \frac{I_s}{0.6eA_p} \sqrt{\frac{M_i}{k_b T_e}}$$
[4.15]

where I_s is the ion saturation current; A_p is the effective area of the probe, M_i is the mass of molecules; k_B is the Boltzmann's constant; e is the electron charge and T_e is the electron temperature.

The ion density at the sheath border (x = d as show in Fig. 4.2) is determined as follow:

$$n_i(d) = n_e(d) = n_{i0} \exp\left[\frac{V_P(d)}{T_e}\right] \approx 0.6n_{i0}$$
 [4.16]

where n_i is ion density in the sheath region; n_e is electron density and n_{i0} ion density in the bulk plasma.

From equation 4.4, the plasma density is directly related to the microwave power absorbed. The plasma density increases with the microwave absorbed increases.

4.2.6 Diffusion process

The net flow of charge species in the discharge, especially those flowing down to the substrate, plays a significant role in plasma processing and has drawn the attention of many researchers [Jaco, 1967]; [Sade, 1991]. The random motion of the charged particles results from the spatial variation of charged particle concentration in the plasma environment is called

diffusion of species. This phenomenon is an important factor affecting the etching parameters such as etch rate or etch anisotropy.

In steady state and the absence of electromagnetic forces, the electron (or ion) diffusion in weakly ionization plasma is calculated as follows [Bitt, 2004]:

$$\Gamma_e = -D_e \nabla n_e' \tag{4.17}$$

where Γ_{e} is flux of electrons (ions); $\nabla n_{e}^{'}$ is the gradient of electron (ions) density and the electron (ion) free diffusion coefficient D_{e} is given by:

$$D_e = \frac{k_B T_e}{m_e v_{ce}}$$
[4.18]

where k_B is the Boltzmann's constant, T_e is the electron temperature; m_e is the mass of electron (ion); and v_{ce} is the collision frequency between electrons and neutrons. The electron-neutron collision frequency is given as

$$v_{ce} = n_n \langle \sigma_{ce} x \upsilon_{ce} \rangle \tag{4.19}$$

where n_n is the neutral density; $\langle \sigma_{ce} x \upsilon_{ce} \rangle$ presents the average of the product of collision cross section and electron velocity distribution over the velocity space.

Diffusion with the effect of electric field between the electrons and ions is known as ambipolar diffusion. The electric field is to accelerate the diffusion of the ions and to retard the diffusion of the electrons. Without this electric field the electrons stream out much faster than the ions. So the diffusion rates of both ions and electrons are approximately equalized.

The ambipolar diffusion rate is given as

$$\frac{\delta n_e}{\delta t} = D_a \nabla^2 n_e^{\prime}$$
[4.20]

where $\frac{\delta n_e}{\delta t}$ is the diffusion rate of electrons (ions); $\nabla n'_e$ is the gradient of electron (ions) density

and the electron (ion) free diffusion coefficient D_a is given by:

$$D_{a} = \frac{k_{B}(T_{e} + T_{i})}{m_{e}v_{ce} + Cm_{i}v_{ci}}$$
[4.21]

In a weakly ionized discharge, the ambipolar diffusion can be simplified as follow:

$$D_a \approx D_i \left(1 + \frac{T_e}{T_i} \right) \tag{4.22}$$

Since $T_e >> T_i$ in weakly ionized plasma, then the ions and electrons both diffuse at a rate that is larger with the ion free diffusion rate, but less than D_e .

In the low pressure, sub-mTorr to a mTorr limit where ambipolar diffusion losses to the walls dominate over volume recombination (the ions more essentially collisionless), the diffusion of species is expressed as [Hopw, 1988]:

$$D_a \nabla^2 n = 0 \tag{4.23}$$

where D_a is ambipolar diffusion coefficient and n is the ion density.

The ambipolar diffusion coefficient is much larger than the ionization rate and the solution for Equ. 4.28 as follow:

$$n(r,z) = \left(\frac{2n_0b}{a}\right) \sum_{n=1}^{\infty} J_1\left(\frac{x_nb}{a}\right) J_0\left(\frac{rx_n}{a}\right) \frac{\exp\left(-\frac{zx_n}{a}\right)}{\left[x_n J_1^2(x_n)\right]}$$

$$[4.24]$$

where a is the chamber radius, b is the discharge radius (Fig. 4.3), J_n is the order nth Bessel function of the first kind and x_n is the nth zero of J_0 .

4.3 Plasma Etching Mechanism

Plasma-assisted etching refers to etching of solids in reactive gas glow discharges in which volatile products are formed, regardless of the apparatus used or the region of the parameter space involved. Plasma-assisted etching plays an important role for diamond postprocessing especially for micro or nanometer structure patterning. There are some unique properties of plasmas-assisted etching that make it useful for material processing and etching. Electrons in low pressure plasmas are not in thermal equilibrium with the ions and neutrons so they can reach higher temperatures. The high electron temperatures in plasmas produce enhanced chemical reaction rates. Another feature of plasma-assisted etching is that energetic ions can be accelerated directionally to the substrate surface with an independent bias source enabling anisotropic etching.

The basic steps of plasma etching take place as following: (1) the radical and ions species are generated by the plasma discharge. (2) The radical species diffuse around the chamber and also toward the substrate. (3) The energetic ions are accelerated by the electric field in the sheath and the strike onto the substrate. (4) Surface reactions. (5) Desorption of the etch products. There are four main categories for the mechanism of plasma etching:



Figure 4.5: The mechanisms of plasma etching [Mano, 1989]

physical etching (or sputtering), pure chemical etching, ion enhanced energetic etching and ionenhanced inhibitor etching as shown in Fig. 4.8. The details of these process have been explained in the research literature [Chap, 1980], [Mano, 89], and [Suga, 1998]. Figure 4.5 summaries these processes as following:

4.3.1 Sputtering:

Sputtering is a process to remove the material by colliding ions into the substrate surface resulting in removal of atoms or group of atoms. This process is dominated by the acceleration of energetic ions formed in the plasma to the substrate surface at relatively high kinetic energy. Some of this energy is transferred to the substrate resulting in material being ejected from the surface as shown in Fig. 4.5a. A qualitative picture of the sputtering process on the substrate surface looks as follows. An impinging ion undergoes a series of collisions on the surface and atoms that rebound with sufficient energy undergo secondary collisions, thereby creating another generation of rebounded atoms. Both the ion itself and energetic rebound atoms have the possibility of getting scattered back through the surface by a series of collisions from a depth that can be a certain fraction of the total ion range. These back-scattered ions and energetic rebound atoms are ejected from the surface [Ande, 1968]. The etch rate, $R_{sputter}$, is directly proportional to the sputtering yield γ (defined as the number of atoms or molecules ejected per incident ion) given by [Maha, 1999]:

$$R_{sputter} = 6.22 \ \frac{\cancel{y}}{\cancel{W}} \ (nm/min)$$
[4.25]

where γ is the sputtering yield; j is the ion flux (mA/cm²); W is the molecular weight of the etched material (g/mol), and ρ is the density of the material to be etched (g/cm³).

The sputter yield is dependent on the energy of the injected ion, the masses of the colliding atoms and the bonding energy of the materials. In general, the ions with energy above 20-30 eV can sputter atoms from a surface. For ion bombardment energy up to 1 kV, the sputter yield is calculated as follow [Sigm, 1969]:

$$\gamma = \frac{3\alpha}{4\pi^2} \frac{4m_i m_t}{(m_i + m_t)^2} \frac{E}{E_b}$$
[4.26]

where m_i is the ion mass; m_t are the masses of the colliding atoms; α is the monotonic increasing function that depends on the atom mass ratio; E_b is the surface binding energy of the material to be etched.



Figure 4.6: Sputtering Yield versus Ion Energy

The value of surface binding energy for diamond substrate is $E_b = 6.67$ eV [Kudr, 2004]; and E is the energy of the incident ion in eV. Figure 4.6 shows the sputtering yield versus argon energy for diamond and silicon substrate [Guzm, 2006].

The use of ion energies above 1 kV is not common in etching discharges because those ions will be implanted in the solid surface. Argon or another noble gas is usually used to create the discharge for sputtering. The sputtering yield increases rapidly with energy up to a few hundred electron volts. For the physical sputtering process, argon ion energies are typically at 500-1000 eV. The etch rate by the sputtering process is often low because the yield is typically of the order one atom per incident ion, and the ion flux incident on surfaces in discharges is often

small. The sputtering from bombardment by ions that arrive directionally perpendicular with the surface result in the etch profiles being vertical or anisotropic.

Some drawbacks of the sputtering process are it causes a rough surface morphology, trenching, mask erosion and poor selectivity. Trenching is the enhanced erosion around the foot of an etched wall. Trenching results from the increased flux of ions at the trenches due to reflection off the side walls as shown in Fig. 4.7. The mask itself can also be removed by the sputtering process, resulting in the final dimension of the opening mask being larger than the initial dimension. This leads to a tapered profile.



Figure 4.7: Typical profile of trenching and mask erosion after sputtering by an inert ion.

Selectivity in sputtering typically decreases with increasing ion energy [Flam, 1989]. The etch product formed from the sputter process is usually a non- volatile compound that may reflected back to the substrate surface. This can roughen the surface and reduce the removal rate.

Sputtering yield is also depended on the oblique incident (angle θ) of the ions [Sigm,1969].

$$\gamma_{\theta} \approx \gamma (\cos \theta)^{-f} \quad (1 < f < 2)$$

$$[4.27]$$

where γ is the sputter yield for perpendicular incident and γ_{θ} is the sputter yield of oblique incident ion.

The most important factor causing an oblique incident angle is the collision of the ions with the gas molecules in the ion sheath. The thickness of the ion sheath depends on the electron density, the electron temperature and the RF bias as shown in equation 4.9. The collision rate between the ions and the molecules also depends on the pressure. So in order to have perpendicular incident ions for anisotropic profile, the pressure should be low or the thickness of the ion sheath should be small.

4.3.2 Chemical Etching:

The pure chemical etching process is shown in Fig. 4.5b. The plasma produces the reactive species by dissociating molecules from the feed gas mixture. The chemical etching process relies on the formation of reactive species in the plasma that adsorb to the surface, react with the surface material to be etched, form volatile etch products and then desorbed from the surface. In the case of diamond etching with oxygen plasma, the chemical etching process occurs when diamond is converted to gaseous carbon monoxide and/or carbon dioxide by

oxidation. The chemical removed rate is dependent on the ability of the process to form and evaporate the etch products (volatility).

Theoretically, the reaction rate is calculated based on the Arrhenius's equation:

$$K(T) = A(T).\exp\left(-\frac{E}{k_B T}\right)$$
[4.28]

where K(T) is the reaction rate coefficients; A(T) is the collision frequency of reactants, T is the substrate temperature, E is the activation energy and k_B is the gas Boltzmann constant.

Since the species in a discharge are almost are neutrals, the flux of the neutral species to the substrate is significantly larger than the ion flux. Because the higher neutral flux, the potential exists for the chemical etching rate to exceed the sputtering rate. The purely chemical etch process is isotropic because the gas-phase etchants arrive at the substrate with a near uniform angular distribution. Therefore, one normally expects a relatively isotropic etch rate [Lieb, 1994]. Chemical etchings processes can produce different etch rates for mask and substrate materials because of chemical reactions difference. So for chemical etching, the etch selectivity is high by choosing mask materials that are less or non-reactive with the plasma radicals.

4.3.3 Ion Enhanced Energetic Etching:

The ion enhanced energetic etching has the advantages of both physical and chemical etching process as shown in Fig. 4.5c. The combine effect of both energetic ions and radical neutrals can be much larger than each separate ion or radical etching process alone [Flam, 1989]. To understand the ion-enhanced energetic etching process consider that non-volatile etch products are formed on the surface or that surface compounds are partly dissociated but are still bounded to the surface. These surface bounded products or compounds will limit the reactions possible for the fresh neutral radicals arriving at the surface. The energetic ions arriving at the surface break these surface bonds exposing the atoms of the substrate to the neutral radicals, increasing its reactivity. The mechanism of ion enhanced energetic etching (ion-assisted etching) is explained by the reactive spot model [Tach, 1983]. First, the active radical species from the plasma are adsorbed onto the substrate surface; after that the energetic ion is accelerated through the sheath and bombards the surface. The ion is injected in the surface and under goes repeated elastic and non elastic collisions with atoms in the substrate. The ion energy is transformed to lattice oscillations and is finally given to the radicals adsorbed on the surface with the result that desorption occurs. Therefore the chemical etching is promoted by one injected ion. The etch rate in this process increases when the ion energy is increased beyond a certain threshold of a few electron volts determined by the properties of the substrate material e.g., the bonding energy. Because the energetic ions strike the surface with a highly directional angular distribution, the etching by this process is highly anisotropic. But the selectivity may be lower compared with the chemical etching.

4.3.4 Ion-enhanced inhibitor etching:

The ion enhanced inhibitor etching process involves an inhibitor species or polymer like material forming from nonvolatile etching products or a film forming from precursors that adsorb during the etching process. The role of ion bombardment is to clear the inhibitor from horizontal surfaces but not the side walls. The inhibitor film, which is deposited on the sidewalls, is not removed because these surfaces only intercept the few ions that are scattered as they cross the sheath. With proper optimization, a highly anisotropic etch with vertical sidewalls can be formed using the ion-enhanced inhibitor etching process. However, the process may not be as selective as chemical etching.

4.4 Surface interactions of plasma etching:

There are two main parts of plasma etching: 1) the plasma environment and 2) the surface interactions. The plasma environment part was briefly introduced in section 4.2 above and it will be developed in more detail below. The process of surface interactions describes the formation of etchant species and how they react on the surface.

4.4.1 Generating etchant species:

In plasma etching, it is necessary to generate the ions and active neutral species which bombard and react with the substrate. They are lost by reaction and recombination processes. Electrons get energy from the electric field, and then via inelastic electron-neutral collisions, they maintain the supply of ions and radical species for the plasma discharge. Thus, collisions involving electrons play a critical role in generating and maintaining the species in the discharge. In oxygen plasma discharges, there are two electron impact reactions which are very important to generating ion and neutral species as follows

$$e + O_2 \rightarrow O_2^+ + 2 e$$
 [4.29]

$$e + O_2 \rightarrow O + O \tag{4.30}$$

In the ionization process, a bound electron in an atom is ejected from that atom. The electrons produced by the ionizing collision above can then be accelerated and collide with other atoms and the multiplication ionization process keeps maintaining the discharge. In addition to ionization the electrons also cause dissociation [Equ. 4.30] and the excitation [Equ. 4.31-4.33]. This excitation process can result in emission of photons which appears as a glow of the discharge.

$$e + O_2 \rightarrow O_2^* \tag{4.31}$$

$$O_2^* \to hv$$
 [4.32]

$$e + O_2 \rightarrow 2O^{\uparrow}$$
 [4.33]

÷

$$O^* \to hv$$
 [4.34]

where O_2^* and O^* are the excited states of O_2 and O. Numerous other chemical reactions can occur when more than one processing gas is flowed into the chamber.

For diffusion of neutral species, the charge free species are assumed to be hard spheres with a constant cross section, the diffusion coefficient for molecule A collided with molecules B is roughly calculated as follow [Lieb, 1994]:

$$D_{AB} = \frac{\pi}{8} \lambda_{AB} \upsilon_{AB}$$
 [4.35]

where λ_{AB} is the mean free path; and ν_{AB} is the mean speed of relative motion and is given by

$$\upsilon_{AB} = \left(\frac{8eT_g}{\pi M_R}\right)^{\frac{1}{2}}$$
[4.36]

where T_g is the gas temperature; and M_R is the effective reduced mass.

The mean free path is the average distance travelled by a particle before colliding and is given by

$$\lambda_{AB} = \frac{1}{n_B \sigma_{AB}}$$
[4.37]

where n_B is the density of B molecules and $\sigma_{AB} = \pi \left(r_A + r_B \right)$ is the collision cross section of

A as seen by B molecules; r_A and r_B are radii of A and B particles.

4.4.2 Adsorption and desorption process

After the etchant species are generated in the plasma discharge, they diffuse or flow to the surface to be etched. These etchant radical species can be absorbed on the surface, produce reactions on the surface, and then the etch products can be desorbed from the surface. The desorbed products flow back to the gas phase. However this is a dynamic process where etchants also can desorbs without reaction or etch products in the gas phase can adsorb back onto the surface.

In a most general description, adsorption is the reaction of molecules with a surface and desorption is the reverse reaction process. A simple reaction of these two reaction processes is

$$A + S \rightarrow A:S \text{ And } A:S \rightarrow A + S$$
 [4.38]

where A is the molecule and S is the surface. A:S designates that molecular is adsorbed on surfaces. Adsorption includes two different categories: 1) Physisorption is a process due to the weak attractive van der Waals force between a molecule and a surface [Kreu, 1986]; and 2) Chemisorption is due to the formation of a chemical bond between the atom or molecule and the surface [Schr, 1971].

Physisorbed molecules are often so weakly bound to the surface that they can diffuse rapidly along the surface. The change in enthalpy $|\Delta H|$ of physisorbed molecules around 1-25 kJ/mol is much less than from chemisorption (~40-400 kJ/mol). Chemisorption of molecules that

has bonds in the gas phase can occur with the breaking of one bond as the molecule bonds to the surface. It can be shown in follow reaction:

$$A=B+S \to AB:S$$

$$[4.39]$$

Followed by the reaction.

$$AB + S \rightarrow A:S + B:S$$
 [4.40]

This process is call dissociative chemisorptions and requires two adsorption sites.

The flux of molecules that are adsorbed is given by [Lieb,1994]:

$$\Gamma_{ads} = \frac{1}{4} sn_{AS} \bar{v}_{A}$$
[4.41]

where n_{AS} is the gas phase volume density of molecules at the surface, \overline{v}_A is the mean speed of the molecules and s is the sticking coefficient, which is a function of the surface temperature. The sticking coefficient for different reactions can have a wide range of

 10^{-6} - 1 and it strongly depends on crystal orientation and surface roughness [Morr, 1984].

In thermal equilibrium, the two reactions of adsorption and desorption must balance. The desorption rate constant can be calculated as follows [Zang, 1988]:

$$K_d = K_0 \exp\left(\frac{-\varepsilon_d}{k_B T_s}\right)$$
[4.42]

where: ε_d is the energy to desorb a species from the surface. K_0 is the number of attempted escapes per second from the adsorption well and T_s is the substrate temperature. Typically, K_0 is around 10^{14} to 10^{16} s⁻¹ for physisorption and 10^{13} to 10^{15} s⁻¹ for chemisorp process. Another important quantity is the percentage of the surface covered with adsorbed species. The quantity is indicated as θ surface coverage.

4.4.3 Chemical kinetics:

Many chemical reactions proceed in stages or steps involving a series of elementary processes. The series of elementary reactions leading from reactants to products is called the mechanism of the reaction. The most important elementary reactions are uni-molecular ($A \rightarrow$ products), bimolecular ($A+B\rightarrow$ products) and termolecular ($A+B+C\rightarrow$ products). The reaction rate R is an important parameter used in chemical reaction kinetic and it is defined as:

$$\mathbf{R} = \frac{1}{\alpha_j} \frac{dn_j}{dt} \text{ for all j;}$$
[4.43]

where n_j is the volume density of molecules of the jth substance and α_j is the stoichiometric coefficient with the negative value for reactants and positive for products. A significant effort in chemical kinetics has been to determine the set of elementary reactions with stoichiometric coefficient. Consider a chemical reaction in a closed system such as

$$3A + B \rightarrow 2C + 4D$$
 [4.44]

The stoichiometric coefficients for this reaction are: α_1 =-3, α_2 =-1, α_3 =2, α_4 =4.

In general, the reaction rate R is determined as follows:

• For unimolecular reaction:

$$\mathbf{R} = -\frac{dn_A}{dt} = \mathbf{K}_1 n_A; \qquad [4.45]$$

• For biomolecular reaction:

$$\mathbf{R} = -\frac{dn_A}{dt} = -\frac{d_B}{dt} = K_2 n_A n_B$$
[4.46]

• For termolecular reaction:

$$\mathbf{R} = -\frac{dn_A}{dt} = -\frac{d_B}{dt} = -\frac{dn_C}{dt} = K_3 n_A n_B n_C$$
[4.47]

The constants K_1 , K_2 , and K_3 are the first, second and third order rate constant respectively. They are functions of the temperature but are independent of the densities as described in equation 4.48.

The rate coefficient can be transformed into linear form as follow:

$$\ln(K(T)) = \ln(A) - \frac{E}{k_B T}$$
[4.48]

Since E, activation energy, is always positive, the negative slope $\frac{-E}{kB}$ indicates that K(T)

increases with T increase and decreases with 1/T increase.

4.4.4 Surface kinetic models:

The gas-solid reactions that occur on the surface are the most important processes for plasma etching. There are two mathematical models used to calculate the reaction rates (gas-solid reactions) occur on the surface.

The first simple model was developed by Langmuir to treat the single site surface reaction mechanism and later modified by Hinshelwood to treat the dual site mechanism. This model is called Langmuir-Hinshelwood kinetic model [Mase, 1996]. The assumptions for this model are: 1) The surface of the adsorbent is uniform, that is all the adsorption sites are equivalent. 2) Adsorbed molecules do not interact. 3) The surface is not fully covered by a mono layer of adsorbed species. 4) One molecule is adsorbed per active site due to a strong valence bond.

To illustrate the Langmuir-Hinshelwood model consider the adsorption and desorption of two gas molecules A and B on a surface S. The reactions occur as follows:

K _a	
$A + S \iff A:S$	[4.49]
K _{d1}	
K _a	
$B + S \iff B:S$	[4.50]
K _d	
K _r	
$A:S + B:S \rightarrow AB + 2S$	[4.51]

The rate equations are

$$\frac{dn_{AS}}{dt} = K_{a1} (1 - \theta_A - \theta_B) (n_{AS} + n_{BS}) - \theta_A K_{d1} n_{AS}$$

$$[4.52]$$

$$\frac{dn_{BS}}{dt} = K_{a2} (1 - \theta_A - \theta_B) n_{BS} - \theta_B K_{d2} n_{BS}$$

$$[4.53]$$

The surface fractions covered with A and B molecules in thermal equilibrium are θ_A and θ_B and from the Langmuir isotherm equation they are [Lieb, 1994]:

$$\theta_{A} = \frac{K_{A}n_{AS}}{1 + K_{A}n_{AS} + K_{B}n_{BS}}$$
[4.54]

$$\theta_{\rm B} = \frac{K_B n_{BS}}{1 + K_A n_{AS} + K_B n_{BS}}$$
[4.55]

where $K_A = \frac{K_{a1}}{K_{d1}}$ is ratio between the rate constant for adsorption K_{a1} and the rate constant for

desorption K_{d1} , n_{AS} is the rate adsorption of molecules A on surface S and n_{BS} is the rate adsorption of molecules b on surface S.

And $K_B = \frac{K_{a2}}{K_{d2}}$ is ratio between the rate constant for adsorption K_{a2} and the rate constant for

desorption K_{d2}

The rate of production of AB is

$$R_{AB} = K_r n_0^2 \theta_A \theta_B$$
[4.56]

At low pressure, $K_A n_{AS} \, \ll \, 1$ and $K_B \, n_{BS} \, \ll \, 1$, the kinetic reaction is second order, then

$$R_{AB} = K_r \frac{K_{a1} K_{a2}}{K_{d1} K_{d2}} n_0^{2} n_{AS} n_{BS}$$
[4.57]

The second model of the surface reaction mechanism involves the reaction of adsorbed A directly with a bombardment molecule B from the gas phase. This model is called the Eley-Rideal kinetics. One or both molecules must be highly reactive. This model is expressed as follows:

$$K_{a}$$

$$A + S \iff A:S$$

$$K_{d}$$

$$K_{a}$$

$$B + S \iff B:S$$

$$K_{d2}$$

$$K_{r}$$

$$(4.58)$$

$$(4.59)$$

$$A:S+B \rightarrow AB+S$$
 [4.60]

Assuming that the reaction itself is the rate-limiting step, the rate equation is then:

$$R_{AB} = K_r n_0 \theta_A n_{BS}$$
[4.61]

where n_{O} is the surface site area density.

At low pressure, the kinetic reaction is second order, and the rate of production is:

$$R_{AB} = K_r K_A n_0 n_{AS} n_{BS}$$
[4.62]

4.4.5 A simple empirical model for diamond etching:

A simple model to calculate the diamond etch rate based on the theory of plasma etching is presented in this section. Diamond can be etched by oxidation to form CO or CO_2 using an oxygen plasma. So oxygen atoms and ions produced from an oxygen discharge is the key factor to remove diamond. The additive of an inert (argon) gas at a small flow rate (6 sccm) in the gas mixture is mainly to help stabilize the plasma discharge and provide ions for the ion assisted etching process [Flam, 1989].

Diamond is reactive ion etched by an oxygen plasma in two steps [Neve, 2001]:

1) Formation of graphite;

$$C_{dia} + O \rightarrow CO_{ads}$$
 (adsorbed carbon monoxide) [4.63]

$$CO_{ads} + CO \rightarrow C \text{ (graphite)} + CO_2 \uparrow$$
 [4.64]

2) Oxidation of the graphite;

$$C + O \rightarrow C:O$$
 [4.65]

$$Ion + C: O \to CO^{\uparrow}$$

$$[4.66]$$

Diamond also is sputtered by the energetic oxygen ions as follows:

$$\operatorname{Ion} + \mathrm{C} \to \mathrm{C} \uparrow$$
 [4.67]

Equation 4.68 describes the adsorption of O atoms on the surface that reacts with diamond (C_{dia}) to form adsorbed carbon monoxide. Equation 4.69 describes the reaction between adsorption carbon monoxides to form carbon (graphite) and CO₂ (gas out). The carbon (graphite) then reacts with oxygen atoms to form a surface carbon-oxygen bond as given in equation 4.70. Equation 4.71 represents the ion assisted desorption in the case of reactive ion etching. And the last equation shows the sputter of diamond by energetic ion bombardment on the surface. A considerable amount of effort has been make to unravel the ratio of CO/CO₂ products forming from oxidative diamond etching by [Lain, 1963], and [Arth, 1951]. Researcher came to a consensus that oxygen chemisorbed on a diamond surface desorbs as CO and to a lesser extent as CO₂ according to [Thom, 1992] and [Ando, 1993]. An approximate volume density ratio of $\frac{CO}{CO_2}$ = 300 is suggested for low pressure processes [Chak, 1995]. So we can

neglect the forming of the CO_2 product from the chemical etching of diamond.

A simple model of the reactive ion etching diamond based on the Langmuir-Hinshelwood kinetic model is shown in Fig. 4.8. There are two main processes that contribute to the removal of diamond from the surface: a) by the flux of positive oxygen ions physically bombarding on the surface and removing carbon by sputtering or ion enhanced etching; and b) by O atoms reacting with the C on the surface and chemically forming the C:O bonds, then desorbing as CO molecules.

Let us assume that the fraction of surface site θ , covered with C:O bonds, has a surface site area density n_0' . And the fraction of uncovered C:O surface is (1- θ) where the oxygen atoms incident on the surface are assumed to react with C to form C:O or the energetic ions sputter on the surface to release carbon atoms.



Figure 4.8: A simple of diamond etching model

We assume that n_{0S} is the density of the oxygen atoms in the gas phase at the surface and n_{iS} is the oxygen ion density at the plasma sheath edge. The flux of oxygen atoms adsorbing on the surface is proportional to the fraction of sites uncovered area (1- θ), so the flux of CO forming from chemical reactions on the surface is calculated as follow [Lieb, 1994]:
$$\Gamma_{ads} = K_a n_{OS} n_0^{\prime} (1 - \theta)$$
[4.68]

The flux of CO atoms desorbed from the surface (by thermal desorption) is:

$$\Gamma_{desorl} = K_d n_0'(\theta) \tag{4.69}$$

The flux of CO atoms desorbed from the surface (by ion assisted) is:

$$\Gamma_{desor\,2} = Y_i K_i n_{iS} n_0(\theta) \tag{4.70}$$

The sputtering process causing the flux of C that is ejected from the surface:

$$\Gamma_C = \gamma_i K_i n_{iS} n_0$$
[4.71]

where K_i is the rate constant for ions incident on the surface, γ_i is the physical sputtering yield and Y_i is the rate desorption.

The steady state condition for CO flux (adsorbs and desorb) is:

$$\Gamma_{ads} = \Gamma_{desorb1} + \Gamma_{desorb2} \Longrightarrow K_a n_{OS} n_0^{'} (1-\theta) = \left(K_d + Y_i K_i n_{iS}\right) n_0^{'} \theta \quad [4.72]$$

The surface coverage is then obtained as equation below:

$$\theta = \frac{K_a n_{OS}}{\left(K_a n_{OS} + K_d + Y_i K_i n_{iS}\right)}$$

$$[4.73]$$

The vertical etch rate R_V is assumed to be flux of desorbed CO (Γ_{CO}) and flux of C ejected by the sputtering process (Γ_C).

$$R_{V} = \frac{\Gamma_{CO} + \Gamma_{C}}{n_{C}}$$
[4.74]

where $n_{\rm C}$ is the carbon atom volume density.

The CO desorption flux is calculated from equation 4.69 and 4.70 as follow:

$$\Gamma_{CO} = \left(K_d + Y_i K_i n_{iS}\right) n_0^{\prime} \theta$$
[4.75]

Rewriting Equ.4.79 gives the etch rate as

$$R_{V} = \frac{n_{0}}{n_{C}} \left[(K_{d} + Y_{i}K_{i}n_{iS})\theta + \gamma_{i}K_{i}n_{iS} \right]$$

$$[4.76]$$

Replace θ from Equ. 4.78, Equ.81 becomes:

$$\mathbf{R}_{\mathbf{V}} = \frac{n_{0}}{n_{C}} \left[\frac{\left(K_{d} + Y_{i}K_{i}n_{iS}\right)K_{a}n_{OS}}{K_{a}n_{OS} + K_{d} + Y_{i}K_{i}n_{iS}} + \gamma_{i}K_{i}n_{iS} \right]$$

$$[4.77]$$

$$R_{V} = \frac{n_{0}'}{nC} \left[\frac{K_{a}n_{OS}}{1 + \frac{K_{a}n_{OS}}{K_{d} + Y_{i}K_{i}n_{iS}}} + \gamma_{i}K_{i}n_{iS} \right]$$

$$[4.78]$$

$$(1) + (2)$$

We can see the etch rate is included two parts: 1) etch rate from reactive ion etching process and 2) etch rate from pure physical sputtering process.

In order to calculate the etch rate from equation 4.78, the rate constants of adsorption, desorption and other quantities like ion and neutral densities need to be determined. First the expression for the adsorption rate coefficient K_a is given [Lieb, 1994]:

$$K_a = \frac{1}{4n_0'} \left(\frac{8k_B T_0}{\pi M_0}\right)^{1/2}$$
[4.79]

where n_0 is the surface site area density; T_0 and M_0 are the neutral gas temperature and the mass of oxygen atom respectively.

Taking the surface state area density for diamond (n_0) as 1.57 x $10^{19}m^{-2}$ [Pate, 1986]. The density of atomic oxygen is calculated using the gas law relations:

$$\frac{P_1}{n_1 T_1} = \frac{P_2}{n_2 T_2}$$
[4.80]

where P_1 is the atmospheric pressure; n_1 is the oxygen molecular density at atmospheric and T_1 is the ambient temperature (300 K). P_2 , n_2 and T_2 are the processing pressure, the oxygen molecular density inside plasma, and the gas temperature (350 K) respectively.

At atmospheric pressure, the oxygen molecular density fill in the process chamber is:

$$n_1 = \frac{6.022 \times 10^{23}}{0.0224} = 2.68 \times 10^{25} \, m^{-3}$$
[4.81]

So from Eq. 4.85, at 4 mTorr of processing pressure, assuming a gas temperature T_2 of 350 K, the oxygen molecular density is:

$$n_2 = \frac{n_1 T_1 P_2}{P_1 T_2} = \frac{2.68 \times 10^{25} \times 300 \times 5.26 \times 10^{-6}}{1 \times 350} = 12.08 \times 10^{19} \, m^{-3}$$
[4.82]

It is assumed that the oxygen molecules are dissociated inside the discharge and 10% of them remain in the form of neutrals at the diamond surface. Hence the oxygen neutral density n_{os} is assumed to be $12.08 \times 10^{18} m^{-3}$.

The value of K_a is:

$$K_{a} = \frac{1}{4n_{0}'} \left(\frac{8k_{B}T_{0}}{\pi M_{0}}\right)^{1/2} = \frac{1}{4x1.57x10^{19}} \left(\frac{8x1.38x10^{-23}x350}{3.1416x16x1.67x10^{-27}}\right)^{1/2}$$

$$K_{a} = 1.08 \ 10^{-17} \ m^{3}s^{-1}$$

 K_d is the rate constant for thermal desorption of CO. It is related to the binding energy and the substrate temperature as follows:

$$K_d = K_0 \exp\left(\frac{-E_b}{k_B T_s}\right)$$
[4.83]

where K_0 is the number of attempted escapes per second. For chemisorptions process, K_0 is range from 10¹³ to 10¹⁵ s⁻¹. The binding energy for the diamond crystal E_B is approximately calculated to be 3.26 eV per bond [Ohat, 1960].

Assuming K_0 is 10¹⁴ s⁻¹ and the value of T_s is 293 K degree then K_d is calculated to be:

$$K_d = 10^{14} \exp\left(\frac{-3.26eV}{8.610^{-5}(\frac{eV}{K})x^{293}K}\right) = 6.5 \ 10^{-43} \ \left(s^{-1}\right)$$

The rate constant for ions incident on the surface K_i is related to the sheath Bohm velocity and the electron temperature T_e as follow:

$$K_{i} = \frac{u_{B}}{n_{0}} = \frac{1}{n_{0}} \left(\frac{k_{B}T_{e}}{M_{i}}\right)^{1/2}$$
[4.84]

The diamond surface density n_0' is $1.57 \times 10^{19} m^{-2}$. The electron temperature T_i is approximately 4 eV and the oxygen ion mass is 16.

So
$$K_i = \frac{u_B}{n_0} = \frac{1}{1.57 \times 10^{19}} \left(\frac{1.38 \times 10^{-23} \times (4 \times 11605)}{16 \times 1.67 \times 10^{-27}} \right)^{1/2} = 3.11 \times 10^{-16} m^3 s^{-1}$$

The yield of the CO molecules desorbed per incident ion on a fully covered surface depends on the ion energy E_i . The factor giving the efficiency of bond breaking by the incident ion is η (($\eta \le 1$) and the energy that binds the molecule (oxygen) to the diamond surface is E_b [Lieb, 1994]. A crude model is that $Y_i \approx \eta \frac{E_i}{E_b}$. Assuming the ion enhanced sputter desorption yield $Y_i \approx 2$.

The value for the oxygen ion density on the diamond surface is assumed to be $n_{iS} = 4x10^{16}m^{-3}$. The atomic volume density of the diamond is known as $1.79x10^{29}m^{-3}$.

Usually the sputter yield factor γ_i for carbon is quite small so the diamond etch rate in an oxygen plasma can be modified from Equ. 4.78 as:

$$R_{V} = \frac{n_{0}}{n_{C}} \left[\frac{K_{a}n_{OS}}{1 + \frac{K_{a}n_{OS}}{K_{d} + Y_{i}K_{i}n_{iS}}} \right]$$
$$= \frac{1.57x10^{19}}{1.79x10^{29}} \left[\frac{1.08x10^{-17}x12.08x10^{18}}{1 + \frac{1.08x10^{-17}x12.08x10^{18}}{6.5x10^{-43} + 2x3.11x10^{-16}x4x10^{16}}} \right]$$

 $R_V = 0.882 \text{ x} 10^{-10} x 20.89 (m/s) = 6.63 \text{ } \mu\text{m/hr}$

Thus the empirical model for calculation the diamond etching rate is in good agreement with experimental etching process. The experimental diamond etching rate for oxygen plasma at a pressure of 4 mTorr is in the range from 4 to 8 μ m/hr.

Consider the etching process without the presence of the bias energy, the Equ. 4.78 become

$$R_{H} = \frac{n_{0}}{n_{C}} \left[\frac{K_{a} n_{OS}}{1 + \frac{K_{a} n_{OS}}{K_{d}}} \right]$$

$$= 1.016 \text{ x } 10^{-10} \left[\frac{1.08 \times 10^{-17} \times 12.08 \times 10^{18}}{1 + \frac{1.08 \times 10^{-17} \times 12.08 \times 10^{18}}{6.5 \times 10^{-43}}} \right]$$

$$[4.85]$$

$$R_H = 6.6 \times 10^{-54} \approx 0 \,\mu\text{m/hr}$$

So for the low pressure processing, the purely chemical etching rate is essentially to the zero. This means the energetic ions contribute a critical factor to the etching process.

CHAPTER 5

CHARACTERIZATION OF PLASMA ETCHER

5.1 Introduction

Plasma parameters such as electron density, electron temperature and electron energy distribution function (EEDF) play an important role for understanding and optimizing the etching process. The plasma properties of the Lambda Technologies etching machine were characterized using both visual imaging and the single Langmuir probe (SLP) diagnostics method. The results of this plasma characterization are described in this chapter. These results also help provide an explanation for the etching results presented in Chapter 6.

5.2 Plasma behavior

The discharge or plasma shape varies with the cavity mode operation, which is determined by the short and probe location. And the etching uniformity, which depends on the plasma uniformity, plays an important role in the etching process. So in order to optimize the etching system, the discharge formed in the cavity has been observed in certain operating modes. A reflection mirror is set on the top of the moveable chuck and the plasma is observed through the side window as shown in Fig. 5.1.



Figure 5.1: Plasma shape imaging set up.

For each pressure regime, the plasma shape was observed and recorded for the best plasma shape by a Canon S2 digital camera. The plasma discharge shape was recorded for pressures of 2 mTorr up to 100 mTorr. The plasma shape is observed from below through the side window as shown in Fig. 5.2. The plasma shape images were taken for both the ECR operating configuration and non-ECR operating configuration. The ECR configuration is achieved when the ring of permanent magnets is present. The permanent magnets are removed for the non-ECR configuration.



Figure 5.2: The plasma shape picture as observed from below using a mirror sitting on the substrate holder that is viewed through a window.

5.2.a The ECR plasma behavior



Figure 5.3: The ECR plasma shape variation with the cavity length

Probe = 3.0 cm, Pressure = 10 mTorr, 6 sccm Ar, and microwave power of 300 W.

Figure 5.3 shows the plasma discharge variation for the ECR regime of a operation as the cavity short length in the ECR regime is increased at a pressure of 10 mTorr. It can be seen that the light emission uniformity varies in this case of an ECR plasma for all positions of cavity length because of the magnetic field effect. The plasma looks more uniform at the 21.56 cm position of the short and it changes its shape at different positions.

Figure 5.4 shows the discharge shape versus microwave incident power. The microwave incident power of 500 W is shown in Fig. 5.4 a, and 700 W and 900 W are shown in Fig. 5.4 b-c,

respectively. The lower microwave power created a brighter region around the discharge edge as shown in Figure 5.4 a. High input power created a brighter area in the center.



Figure 5.4: The ECR plasma shape varied with the microwave incident power at a pressure of 4 mTorr and gas flow rate of 10 sccm argon.



Figure 5.5: ECR plasma shapes versus short position and modes

The short position was around TM_{012} for (a-c) and TM_{013} for (d-f) modes with a pressure of 4 mTorr, a gas flow rate of 10 sccm argon, and a microwave power of 700 W.

Figure 5.5 a-c shows the plasma shapes as the short position is varied around the TM_{012} mode. And Figure 5.5 d-f shows the plasma discharge shape as the short position is varied around the position of the TM_{013} mode. The plasma shape has similarity in both cases except that the bright spots around the edge are more pronounced in the TM_{013} mode than in the TM_{012} mode.



(a)

Figure 5.6: Comparison of plasma shape versus different gas mixtures for a pressure of 15 mTorr, a microwave power of 900 W, $L_S = 13.6$ cm, $L_P = 3$ cm.

Figure 5.6 a-b shows the plasma discharge with a gas mixture of $Ar:SF_6 = 10:2$ sccm and Ar:SF₆:O₂= 10:2:20 sccm, respectively. The plasma shapes are the same in both case. The addition of oxygen flow in the $Ar: SF_6$ gas mixture does not significantly effect the plasma shape.

Figure 5.7 a through g shows an argon plasma discharge at pressures of 2, 7, 10, 15, 25, 45 and 100 mTorr, respectively. The plasma images have higher brightness in the center for the pressure regime of 7-25 mTorr. At pressures of 45 and 100 mTorr, the plasma emission intensity is more focused at the edge than in the center.



Figure 5.7: Plasma shape at different pressures for an argon gas flow rate of 10 sccm, a microwave power of 500 W, $L_S = 13.8$ cm and $L_P = 3$ cm.



Figure 5.8: Plasma shape versus microwave power for a gas mixture of Ar:O₂:SF₆= 6:20:2 sccm, a pressure of 4 mTorr, $L_S = 13.3$ cm, $L_P = 3$ cm.

Three different input microwave powers of 500 W, 700 W and 900 W were used to investigate the plasma discharge for a gas mixture of $Ar:O_2:SF_6$ at a pressure of 4 mTorr as shown in Figure 5.8 a-c, respectively. The discharge shape is formed following the magnet field structure present between the alternating magnet poles. The plasma discharge at a microwave power of 700 W shows more uniformity than the ones at 500 W and 900 W.

During the etching process, the reflected microwave power needs to be taken into account. Initially, the operator adjusts the cavity length around a specific mode $(TM_{012} \text{ or } TM_{013})$ location, as shown in Fig. 5.2, to get the minimum reflected power (that means more absorb power into the plasma). A near perfect zero reflect microwave power can be achieved to maximize the energy transfer from the source, however this only lasts a short time because of nature of the dynamic plasmas. How close to zero reflected power needs to maintain for optimizing the etching process is an important question in terms of uniform etching? By

observing the plasma shape with the reflected power less than 15% of the incident power, we can see the microwave reflected power of 34 W or 7 % of the incident power will give better performance in terms of plasma uniformity (Fig. 5.9 c).



Figure 5.9: Plasma shape versus reflected microwave power with a gas mixture of Ar:O₂:SF₆= 6:20:2 sccm, a pressure of 4 mTorr, an incident microwave power of 500 W, $L_S = 17.55$ to 17.7 cm, $L_P = 3$ cm.

When operating an $Ar: O_2: SF_6$ plasma, it is desired to know the best position of the cavity length that gives a plasma shape which appears the most uniform. Figure 5.10 a-d shows the plasma shape variation with cavity length. At a pressure of 45 mTorr, the plasma uniformity is good at L_S=13.7 cm as show in Fig. 5.10 c.





Figure 5.10: Plasma shape versus cavity length with a gas mixture of Ar:O₂:SF₆= 10:20:2 sccm, a pressure of 45 mTorr, an incident microwave power of 900 W, $L_P = 3$ cm.

Based on the images from the plasma etcher operating in an ECR configuration, some keys settings to optimize the etcher system are

- For TM_{013} operation, good plasma uniformity can be obtained at 21.56 cm and 3 cm for the short and probe positions, respectively.
- For TM_{012} operation, good plasma uniformity can be obtained at 13.7 cm and 3 cm for the short and probe positions, respectively.
- A microwave reflected power at 7 % of the incident power give better performance in terms of plasma uniformity.
- 5.2. b The non_ECR plasma behavior:



Figure 5.11: Non-ECR plasma shape versus pressure with argon gas flow rate of 10 sccm, a pressure of 4-100 mTorr, a microwave power of 700 W in the TM_{012} mode.

The non-ECR plasma images show the discharge light emission is more diffuse everywhere in the chamber as compared to ECR plasmas. Figure 5.11 a-f show the plasma discharge variation from 4-100 mTorr for the TM_{012} mode and Fig. 5.12 a-f show the plasma discharge variation from 4-100 mTorr for the TM_{013} mode. Comparing between two non-ECR plasma modes, it is hard to see any difference between the plasma behaviors because of the mode.



Figure 5.12: Non-ECR plasma shape versus pressure with an argon gas flow rate of 10 sccm, a pressure of 4-100 mTorr, a microwave power of 700 W, and aTM_{013} mode.

5.3 Plasma diagnostic using a single Langmuir probe (SLP)

5.3.1 Introduction

The Langmuir probe is a fundamental tool for plasma diagnostics that is used to determine several basic plasma properties, such as the plasma density and the electron temperature. This diagnostic technique is well established and suitable for low pressure gas discharges. It works by inserting one or more electrodes into the plasma. The current density flowing to the surface of the probe tip is measured as a function of the voltage applied to one of the electrodes. This yields an *I-V* characteristic as shown in Fig. 5.13.



Figure 5.13: Single Langmuir probe I-V curve.

By using the SLP diagnostic method, we can measure the ion saturation current I_s , the electron energy distribution function (EEDF), the electron temperature T_e , and the plasma charge density n_e .

5.3.2 The single Langmuir probe structure

The single Langmuir probe structure is shown in Fig. 5.14. The probe electrode is made of tungsten to handle the high temperature from the plasma environment. The probe's radius is 0.406 mm. The probe is enclosed by a quartz tube with a diameter of 5 mm. One of the ends of

the tungsten probe is exposed to the plasma with a length of 2 mm. The other end of the tungsten rod is soldered to a braided steel wire enclosed by another quartz tube with a diameter of 1 cm to increase the mechanical strength.



Figure 5.14: The single Langmuir probe structure

Shrink wrap is placed around the steel wire and the quartz tube base to prevent the internal twisting of the solder joint to the brittle tungsten rod. The shrink wrap is covered by a woven ceramic cloth for heat resistance. The probe is connected to an external measurement

device outside of the chamber through a multi-pin electrical feed through as shown in Fig. 5.16. A wire is connected to the chamber wall (ground).



5.3.3 The single Langmuir probe set up:

Figure 5.15: The single Langmuir probe set up.

The Single Langmuir Probe (SLP) experimental set up for characterization of the plasma etcher is shown in Fig. 5.15. It is constructed of a SLP probe, as described in Fig. 5.14, positioned at a precise location in the discharge by a stainless steel apparatus base. The base sits on the movable chuck holder.



Figure 5.16: The SLP probe measurement diagram.

The probe tip can be positioned at a specific z direction using the movable chuck holder which is controlled by the computer. The positioning apparatus for the SLP probe is shown in Fig. 5.16.

5.3.4 Theory of the SLP:



Figure 5.17: Magnified view of small area near SLP probe.

When the probe is inserted into the plasma region, it is surrounded by a plasma sheath as shown in Fig. 5.17. The thickness of the sheath is of the order of a Debye

length $\lambda_D = \left(\frac{\varepsilon_0 kT_e}{n_e e^2}\right)^{1/2}$. For a low pressure regime, the value of Debye length is typical in the

order of 0.02 mm if the plasma density is $n_e = 8.5 \times 10^{11} cm^{-3}$.

Under conditions that the probe is an open circuit connection, the flux of electrons and positive ions reaching the probe is equally. This condition occurs when the applied probe voltage V_A is equal to the floating potential V_f . When the probe voltage V_A is a large negative, any incident electron will be reflected back into the bulk plasma due to the repulsive force imposed by the probe electric field on those electrons. Thus the electric current is mostly contributed by the ions falling into the probe. When the probe voltage V_A equals the plasma potential V_P , the probe is at the same potential as the plasma, so more electrons reach the probe than the ions due to electrons travel much faster and having a higher energy than the ions. When the probe voltage is greater than V_P and electrons are attracted to the probe. So when the probe voltage is varied from a negative to a positive value, an I-V curve will be measured as shown in Fig. 5.13.

The electron energy distribution function (EEDF) is determined from the second derivative of the I-V curve as follows [Lieb, 1994]. Assuming an electron travels in the bulk plasma with a velocity v. The minimum velocity that an electron must have at the plasma sheath edge to reach the probe is given as

$$v_{\min} = \left[\frac{2e(Vp - V_A)}{m_e}\right]^{1/2}$$
 [5.1]

where V_P is the plasma potential; V_A is the applied voltage probe and m_e is the electron mass.

The electron current normal to a planar probe in Cartesian coordinates is expressed as

$$I_e = eA \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [v_z f_e(v)] d_z d_y d_x$$
[5.2]

where A= $2\pi rl$ is the physical collecting area of the probe and $f_e(v)$ is the electron velocity distribution function.

Equation 5.2 can be rewritten in spherical coordinates with the change of variable $E = \frac{1}{2e}mv^2$ as follow:

$$I_e = \frac{2\pi e^3}{m^2} A \int_{V}^{\infty} E\left\{ \left(1 - \frac{V}{E}\right) f_e[v(E)] \right\} dE$$
[5.3]

Performing a second differential of equation 5.3 with respect to V gives:

$$\frac{d^2 I_e}{dV^2} = \frac{2\pi e^3}{m^2} A f_e[\nu(V)]$$
[5.4]

The electron distribution function (EEDF) $g_e(E)$ is defined as follow:

$$g_e(E) = 2\pi \left(\frac{2e}{m}\right)^{3/2} E^{1/2} f_e[\nu[E]]$$
 [5.5]

Combine equation 5.4 and 5.5, we obtain:

$$g_e(V) = \frac{2m}{Ae^2} \left(\frac{2eV}{m}\right)^{\frac{1}{2}} \left(\frac{d^2I_e}{dV^2}\right)$$
[5.6]

Equation 5.6 shows the value of EEDF $(g_e(V))$ is calculated directly from the measured value of

the second derivative
$$\frac{d^2 I_e}{dV^2}$$
.

Two different EEDF curves include the Maxwellian EEDF and Druyvesteyn EEDF. The normalized Maxwellian EEDF is given as [Perr, 02]:

$$g(\varepsilon) = \left(2.073\right) \left(\frac{3}{2} k_B T_e\right)^{-3/2} \varepsilon^{1/2} \exp\left(-\varepsilon / k_B T_e\right)$$
[5.7]

where ϵ is the electron energy (eV).

The normalized Druyvesteyn EEDF is given below [Gund, 01]:

$$g(\varepsilon) = (1.038) \left(\frac{3}{2} k_B T_e\right)^{-3/2} \varepsilon^{1/2} \exp\left(-0.5471 \frac{\varepsilon^2}{\left(\frac{3}{2} k_B T_e\right)^2}\right)$$
[5.8]

The Maxwellian EEDF assumes: 1) the electron-electron collisions are much more frequent than electron-neutral collisions and 2) the collision frequency is constant versus electron energy.

The Druyvesteyn EEDF assumes 1) the electron-neutral collisions are most frequent and 2) the electron-neutral collision cross section versus electron energy is constant.

The electron temperature is determined by numerically integrating the EEDF as follows:

$$T_e = \frac{2}{3} \sum_{i=1}^{i_{\text{max}}} E_i g(E_i) \Delta E = \frac{2}{3} E_{ave}$$

$$[5.9]$$

where T_e is the electron temperature (eV); and E_{ave} is the average electron energy (eV).

The electron density n_e can be determined from the EEDF distribution function as follows:

$$n_e = \int_0^\infty g_e(\mathbf{E}) d\mathbf{E}$$
 [5.10]

In case of the ion mean free path $\lambda_i \gg \lambda_{De}$ (the Debye length), the charge density is determined by the formula [Perr, 2002]:

$$n_e = \frac{I_s}{(0.61)eAP} \sqrt{\frac{M_i}{eT_e}}$$
[5.11]

where I_s is the ion saturation current, A_p is the effective area of the probe, M_i is the mass of argon atom, and T_e is the electron temperature (V).

The second derivative $\frac{d^2I}{dV^2}$ can be determined by measuring the second harmonic current response of the probe, point by point, to a small applied voltage signal using a Lock-in Amplifier (L.I.A) device.

The next section describes how to derive the second derivative $\frac{d^2I}{dV^2}$ from an I-V curve.

5.3.5 Method to measure the second derivative $\frac{d^2 I}{dV^2}$ from an I-V curve using a Taylor series

expansion

In order to experimental determined the second derivative $\frac{d^2 I}{dV^2}$, the Taylor series is used to

approximate the second derivative of current function. In the I-V curve collected from SLP probe as shown in Fig. 5.13, the current (I) varies as a function of voltage probe V. This function can be expressed by a Taylor series expansion near an applied voltage point V_x .

$$I(V) = \sum_{k=0}^{\infty} \frac{\left[I^{k}(V_{x})\right] [V - V_{x}]^{k}}{k!}$$
[5.12]

where $I^k(V_x)$ is the k^{th} derivative of the current I (V=V_x). If a small sinusoidal signal voltage with an amplitude v is applied to the probe

$$V = \left[V_{\chi} + v\sin(\omega t)\right]$$
[5.13]

And I(V) =
$$I[V_{\chi} + v \sin(\omega t)]$$
 [5.14]

Substituting Equ.5.13 and 5.14 into 5.12, then Equ.5.12 becomes:

$$I(V_x + v\sin(\omega t)) = \sum_{k=0}^{\infty} \frac{\left[I^k(V_x)\right] \left[v\sin(\omega t)\right]^k}{k!}$$
[5.14]

The amplitude of the sinusoidal signal is quite small so the higher order terms the Taylor series expansion are negligible. Equation 5.14 can be simplified and rearranged as follows [Perr, 1994]:

$$\frac{d^2 I}{dV^2} \approx 4 \left[\frac{|I_{2nd}|}{v^2} \right]$$
[5.15]

The small signal second harmonic I_{2nd} is detected and measured by a lock-in amplifier (L.I.A) applied to the measurement circuit.

5.4 The SLP characterization results

This section describes the results from the single Langmuir probe used to characterize the plasma properties produced from the Lambda etcher. An Argon plasma is mostly used for the measurements. Other plasma discharge like oxygen (O_2) and sulfur hexafluoride (SF_6) plasmas will physically damaged the SLP probe and hence were not measured with the SLP.

5.4.1 Electron energy distribution function (EEDF) variation with pressure

Figures 5.18-5.25 show SLP results for the EEDF of the plasma etcher (Ar flow rate of 10 sccm, measured at the base of the discharge (r= 0, z= 0), P= 700 W, TM_{013} modes), for various pressures from 4 mTorr to 45 mTorr.



Figure 5.18: EEDF at pressure of 4 mTorr (ECR).



Figure 5.19: EEDF (semi-log plot) at pressure of 4 mTorr (ECR).



Figure 5.20: EEDF at pressure of 4 mTorr (*non-ECR*)



Figure 5.21: EEDF (semi-log plot) at pressure of 4 mTorr (non-ECR)



Figure 5.22: EEDF at pressure of 10 mTorr (ECR)



Figure 5.23: EEDF (semi-log plot) at pressure of 10 mTorr (ECR).


Figure 5.24: EEDF at pressure of 10 mTorr (non-ECR).



Figure 5.25: EEDF (semi-log plot) at pressure of 10 mTorr (non-ECR).



Figure 5.26: EEDF at pressure of 15 mTorr (ECR).



Figure 5.27: EEDF (semi-log plot) at pressure of 15 mTorr (ECR).



Figure 5.28: EEDF at pressure of 15 mTorr (non-ECR)



Figure 5.29: EEDF (semi-log plot) at pressure of 15 mTorr (non-ECR).



Figure 5.30: EEDF at pressure of 25 mTorr (ECR).



Figure 5.31: EEDF (semi-log plot) at pressure of 25 mTorr (ECR).



Figure 5.32: EEDF at pressure of 25 mTorr (non-ECR)



Figure 5.33: EEDF (semi-log plot) at pressure of 25 mTorr (non-ECR).



Figure 5.34: EEDF at pressure of 45 mTorr (ECR).



Figure 5.35: EEDF (semi-log plot) at pressure of 45 mTorr (ECR).



Figure 5.36: EEDF at pressure of 45 mTorr (non-ECR)



Figure 5.37: EEDF (semi-log plot) at pressure of 45 mTorr (*non-ECR*)

The SLP probe was positioned at the center of the discharge (r=0, z=0). Discharges of magetized (ECR) and non-magnetized (Non-ECR) operating modes were measure using the SLP probe for comparison purposes. The EEDF's of these measurements varied versus pressures of 4, 10, 15, 25 and 45 mTorr as shown in Fig. 5.18 - 5.37. Both Maxwellian and Druyvesteyn curves are also plotted with the same average energy as the experiment plot. The experiment EEDF data point is represented as the dotted data points. For all measurements, the argon gas flow was 10 sccm, the power absorbed in the discharge was 700 W, the power reflected from the microwave cavity was 40-50 W and the excitation probe length L_p was held at 3 cm.

Figures 5.18, 5.19, 5.22, 5.23, 5.26, 5.27, 5.30, 5.31, 5.34, 5.35 shows the EEDF for the magnetized discharges. For a low pressure of 4 mTorr, Fig. 5.19 shows that the measurement data almost fits a Maxwellian profile. The experiment EEDF data generally falls between the Maxwellian and Druyvesteyn curves at higher pressures of 10, 15, 25 and 45 mTorr. The energy distribution with the high energy electron tail depleted may be explained from the increased of electron-neutron collisions at higher pressures.

Figures 5.20, 5.21, 5.24, 5.25, 5.28, 5.29, 5.32, 5.33, 5.36 and 5.37 shows that the EEDF for the non-magnetized discharge fits the Maxwellian distributions curve best for pressures of 4-15 mTorr. At the higher pressures of 25 and 45 mTorrt it falls between the Maxwellian and Druyvesteyn curves especially at higher energies of 15 eV or more. The high energy portion of the electron tail may be depleted as a result of inelastic collisions that deplete high energy electrons.

Thus, at the lower pressures of 4 mTorr, for both non-magnetized and magnet discharges, the EEDF best fits the Maxwellian curve especially for electron energies below 20 eV. For the magnetized ECR discharge, more high energy tail depletion occurs at higher pressures of 10, 15, 25 and 45 mTorr, compared with the non-ECR magnetized discharge.

5.4.2 Plasma density

The charge density measurements were taken over a range of pressures as shown in Fig. 5.38 (for ECR and non-ECR plasmas). The discharge power investigated was 700 W and the argon flow rate was 10 sccm. The probe was located at the center of the chamber r = 0 and it was positioned below the discharge base at a downstream position of 4 cm. There are significant differences in charge density between magnetized and non-magnetized operating modes as seen in Fig. 5.38. The non-magnetized discharge has a higher charge density as compared with the magnetized discharge. Since the plasma discharge cannot be reliably maintained below 4 mTorr without magnets, it can be concluded that the presence of magnetic field reduces charge density but it is beneficial and necessary for operating processes in the very low pressure regime (< 4 mTorr).



Figure 5.38: The plasma density versus pressure. Plasma condition: Ar gas flow rate of 10 sccm, r = 0, z = -4 cm and microwave power = 700 W.

5.4.3. Electron temperature

The electron temperature measured versus pressure is shown in Fig.5.39. The electron temperature values are determined according to equation 5.9 using the E_{ave} values of the SLP measurement. The electron temperature is higher for the non-magnetized plasma as compared

with the ECR plasma. Lower pressures produce high electron temperature plasma due to the longer mean free path of the electrons.



Figure 5.39: The electron temperature versus pressure. Plasma condition: Ar gas flow rate of 10 sccm, r = 0, z = -4 cm and microwave power = 700 W.

5.4.4. Compare of plasma density between the 17.8 cm and 30.5 cm diameter reactor

Figure 5.40 shows the comparison of plasma density versus pressure between two reactor: 17.8 cm [Perr, 2002] and 30.5 cm diameter.



Figure 5.40: Comparison the plasma density versus pressure for two reactors: 17.8 cm and 30.5 cm.

The density plasma from 30.5 cm diameter reactor (used in this research) is higher compare with the 17.8 cm diameter reactor. So the Lambda Technologies etcher with 30.5 cm diameter reactor produces a higher plasma density as compared with the 17.8 cm diameter reactor.

5.5 Summary

Experiments have been performed to develop and characterize the microwave plasma-assisted etcher. Several selected experimental observations were included in the chapter. A summary of several observations include

- The Lambda Technologies etcher operates with microwave resonant modes as expected from earlier work.

The adjustment of the Short and the Probe such that the microwave reflected power was around
7 % of the incident power gave good performance in terms of plasma uniformity.

- The charge density with non-ECR plasma operation is higher than with ECR plasma operation.

- The plasma charge density increased with pressure increases and operated with plasma high densities of $7x10^{11}$ - $3x10^{12}$.

- The electron temperature decreased with pressure increases.

CHAPTER 6

DIAMOND ETCHING EXPERIMENTAL AND RESULTS

6.1 Introduction

Due to the interest in diamond-based electronic devices, MEMS and micro-fabrication applications, plasma etching plays an important in diamond post processing. The Lambda Technologies etcher machine was developed from a previous version of the machine based on designs by Michigan State University. In order to understand the behavior of this plasma etcher machine, several diamond etching experiments were performed. This chapter presents the experimental diamond etching results for the Lambda plasma-assisted etching with focus on four key output parameters: etch rates, anisotropic etching, selectivity and surface smoothness.

6.2 The key plasma-assisted etching reactor input parameters

6.2.1 Microwave power

Microwave power is needed to maintain the ionization process in a gas discharge. More input microwave power in a discharge will increase the ion density on the surface etched following the formula [Lieb, 1994]:

$$P_{abs} = en_{is}u_B A E_T$$

$$[6.1]$$

where P_{abs} is power absorbed by a plasma, n_{is} is the ion density at the sheath edge, A is the area for particle loss and E_T is the total energy lost per ion-electron pair.

$$E_T \approx E_c + E_{sheath} \tag{6.2}$$

Where E_c is the collisional energy loss per ion-electron pair and E_{sheath} is the energy lost associated with an electron and ion crossing the sheath.

Therefore a microwave power input increase is expected to increase the etch rate.

6.2.2 Pressure

The pressure is an important factor in plasma etching. It affects the mean free path of the species and the ion collision frequency. A lower pressure in the process chamber decreases the ions density but increases the electron temperature (see Chapter 5). So the pressure contributes to determining the etch rates. Another important consideration for pressure selection is that lower pressure plasma has few collisions by ions crossing the sheath adjacent to the substrate. The more directed ion flow across the sheath at lower pressure leads the better anisotropic etching.

6.2.3 Gas flow rates

Since the gas mixture used to etch diamond includes argon (Ar), oxygen (O_2) and sulfur hexafluoride (SF_6), the flow rate of each gas affects the etching result. From the theory of etching discussed earlier in Chapter 4, oxygen gas is the most important feed gas to etch

diamond. Generally a higher proportion of oxygen in the gas mixture will increase the etch rate. The total gas mixture flow rate also affects the output etching result. For a given pressure regime, the etch rate often decreases with too low of a gas mixture flow rate. Thus an optimize gas flow rate is required to maintain a high etch rate [Chak, 1995].

6.2.4 RF substrate Bias

The energy of the ions that strike the substrate is very important for both etch rate and anisotropic etching. The kinetic energy of the incident ions is directly influenced by the rf applied bias potential to the substrate. Increasing the bias gives more kinetic energy to the impinging ions which gives an increase of the etch rate.

6.3 Experimental diamond etching results

6.3.1 Effect of the input variables on diamond etching rates:

All the diamond etching experiments used the same conditions with respect to substrate location (z position=-4 cm) and TM_{013} mode. A series of experiments were performed and a normal set of input parameters were determined. The normal input parameters included a pressure of 4 mTorr, a microwave power of 700 W, a substrate bias of -125 V and a gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm. This set of input parameters proved to give good results in terms

of etch rate, anisotropic profile, selectivity and surface roughness. The dependence of the etching results on the various input parameters are described in the following sections.



6.3.1a Microwave power

Figure 6.1: Etch rate versus microwave power. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 300-900 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

The microwave power is an important input variable in determining the diamond etching rate. Increasing the microwave absorbed power increases the ion density at the sheath boundary as described in Eq. 6.1 in previous section. The increased ion density has more ions striking the substrate, which increases the diamond etch rate. The effect of microwave power on the etch rate is shown in Fig. 6.1.

6.3.1 b Pressure

The chamber pressure is another factor affecting the diamond etching rate since it changes the mean free path and collision frequency of the species. The etching rates for nano-crystalline diamond, microcrystalline diamond and single crystal diamond versus pressures are shown in Fig. 6.2. The etching condition was a gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm, a microwave power of 700 W, and a substrate bias of -125 V and the substrate location z = -4 cm.

As we can see the etch rates increase with pressures increases. The microcrystalline diamond (MCD) etch rate is highest as compared with NCD and SCD diamond. The thickness of the SCD diamond substrate is quite larger (~1500 μ m) compared with MCD and NCD (~5-10 μ m). The large thickness of the substrate causes more voltage drop on the surface. This is a factor causing the lower etching rate of SCD diamond.



Figure 6.2: Etch rates versus pressure (ECR). The plasma etching condition included a pressure of 4-45 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

6.3.1 c The substrate induced DC bias

The ion energy is very important for both sputtering and reactive ion etching processes. The RF bias independently applied to the substrate has significant impact on the etch rates by increasing the kinetic energy of the ions bombarding onto the surface.



Figure 6.3: Etch rate versus induced DC substrate bias. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, 0 to-200 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and the substrate location z =-4 cm. An aluminum mask was used.

For the experiment studying the effect of the rf induced dc bias on the diamond etch rate, a pressure of 4 mTorr, a gas mixture $Ar: O_2: SF_6 = 6:20:2$ sccm, and a power of 700 W was used. Figure 6.3 shows the etch rate of nano-crystalline diamond versus induced DC bias. The experimental results show the diamond etching rates increased significantly with bias. For ECR, the etch rates increased from 0.4 µm/hr (0 V) to 10.3 µm/hr (-200 V). And for non-ECR, the etch rates is higher from 1.6 µm/hr (0 V) to 15.1 µm/hr (-200 V). The explanation for this is because the non-ECR plasma has a higher plasma density than the ECR plasma as seen in Chapter 5 section.

6.3.1.d The gas mixture flow rates:

6.3.1.d. 1 Oxygen (O₂) flow rate:

Oxygen is the key factor to remove carbon from the diamond surface through the plasma surface reactions and desorbing CO molecules. Diamond etch rate is expected to vary with the oxygen flow rate in the feed gas composition. Theoretically, a higher proportion of oxygen in the feed gas mixture produces a higher diamond etch rate.



Figure 6.4: Etch rates versus oxygen flow rate (ECR). The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:5-20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

Fig. 6.4 shows the diamond etching rate versus oxygen flow rate (ECR plasma). The diamond substrates were boron doped single crystal diamond. The experiment condition was an argon flow rate of 6 sccm, a pressure of 4 mTorr, a substrate bias of -125 V and a microwave

power of 700 W. The results show that the diamond etch rate increased with increased oxygen flow rate in the gas mixture.





Figure 6.5: Diamond etch rates versus argon flow rate (ECR). The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6-24:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

Argon gas does not participate in reactive ion etching because it is a noble gas. Argon only plasmas result in diamond removal by purely sputtering, and hence the diamond etch rate is very low [Sand, 1989]. The absence of argon in an oxygen based plasma resulted in irreproducible etch rates and non uniform surfaces after etching [Grot, 1992]. In order to understand the effect of argon in the gas mixture, an oxygen flow rate of 20 sccm was kept constant and the argon flow rate was varied from 6 to 24 sccm in the gas composition. Figure 6.5 shows the diamond etch rate versus argon flow rate. The results show that with more argon added to the gas mixture, the diamond etch rate is decreased. We observe that the presence of small amounts of argon (6 - 10 sccm) in the oxygen plasma helps stabilize the plasma during the etching process while maintaining the same etch rate.

6.3.1.d 3 Sulfur hexafluoride (*SF*₆) flow rate:

Sulfur hexafluoride (SF_6) plasmas have been widely used for dry etching silicon based materials and metals (Ti, W). Without SF_6 in the gas mixture, the diamond etched surface appears with a lot of whisker and very rough as shown in Fig. 6.22. So SF_6 gas is added in the oxygen rich gas mixtures to remove the micro-masking forming on the surface etch.

The effect of SF_6 gas on the diamond etch rate is shown in Fig. 6.6. The argon and oxygen gas flow rate in the gas mixture was kept the same at 6 and 20 sccm, respectively. The

 SF_6 gas flow rates were varied from 2 to 10 sccm, resulting in the diamond etch rate decreasing with increased SF_6 gas flow.



Figure 6.6: Diamond etch rate versus SF_6 gas flow rate. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:20:0-10$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

Fig 6.6 shows that SF_6 gas flow rate increases have a negative effect on the diamond etch rate. When adding more SF_6 gas in the range from 6 to 10 sccm gas into the gas mixture, the diamond etch rates significantly decreased. The reason behind the negative effect of SF_6 gas on the diamond etch rate is discussed in work by Mogab [Moga, 1978]. The presence of SF_6 in the feed gas can retard the diamond etch rate due to the [F] atoms produced that can compete with the oxygen atoms at surface sites. Also the [F] ions can react with carbon on the diamond surface to form fluorocarbon [CF_3] radicals. These radicals can react with the oxygen atoms to produce the fluoroxy compounds (e.g., CF_3OOCF_3, CF_3OF ,...) [Moga, 1978]. So the number of oxygen atoms on the etched surface sites may be reduced causing the lower etch rate. Thus in order to maintain the high diamond etch rate and keep the etched surface smooth with the whiskers free, a optimize amount of SF_6 gas from 2 to 3 sccm can be added into the oxygen rich gas mixture. 6.3.2 Effect of the pressure on the anisotropic etching profile



Figure 6.7: SEM cross section image used to measure the anisotropic angle.

Anisotropic etching is an important factor in the etching process. An anisotropic diamond etching process which removes diamond in the vertical direction is very desirable since it will follow the photolithography mask pattern with high accuracy.



Figure 6.8: Anisotropic diamond etching angle versus pressure. The plasma etching condition included a pressure of 4 -45 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

The degree of anisotropy is an angle created by the vertical angle of the etched profile sidewall with respect to the bottom surface as shown in Fig. 6.7. Anisotropic etching angle versus pressure was investigated on NCD samples as shown in Fig. 6.8. High pressures caused a

larger deviation from a perpendicular sidewall feature. Other anisotropic profiles of diamond etching are achieved at a pressure of 4 mTorr as shown in Figs. 6.9, 6.10 and 6.11 for NCD, MCD and SCD, respectively.





Figure 6.9: A highly anisotropic NCD diamond etching profile (SEM image). The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -150 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.


MCD

Figure 6.10.: A highly anisotropic MCD diamond etching profile (SEM image). The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.





Figure 6.11.: A highly anisotropic SCD diamond etching profile (SEM image). The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:1$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

6.3.3 Mask selectivity:

Diamond etching selectivity refers to the ratio between the diamond etch rate compared to the mask material etch rate. A material with high selectivity is needed for masking diamond. For this investigation of mask selectivity, five different mask materials were chosen including gold (Au), aluminum (Al), titanium (Ti), silicon dioxide (SiO₂) and silicon nitride (Si₃N₄). The mask layer is deposited and patterned on a square 1.5 x 1.5 cm² NCD substrate with diamond

thickness \sim 2-4 µm deposited on silicon wafers using the microwave plasma-assisted CVD diamond system at Michigan State University [Tran, 2007].

6.3.3.1 Patterning techniques:

This section describes the patterning techniques used for five different mask materials prior to the diamond etching.

	Equipment	Substrate Temp. (C)	Thickness (nm)
Gold	PVD_E beam evaporation	25	~ 300
Aluminum	PVD_DC sputtering	25	~ 300
Titanium	PVD_DC sputtering	25	~ 1000
SiO ₂	PECVD_low rate	300	~ 2000
Si ₃ N ₄	PECVD	300	~ 1200

Table 6.1: Metallization techniques

The mask materials were deposited on diamond using equipment in the clean room as described earlier in Chapter 3. Table 6.1 shows the specific techniques and the typical film thicknesses deposited on the diamond surface. After the mask material film is deposited on diamond samples, the next step is a lithography process to pattern the diamond samples. A

positive photoresist (PR), Shipley 1813, is used to transfer the pattern the sample using a photolithography mask. First, the 1813 PR is spun on the substrate at 3000 rpm for a time of 30 second to achieve a PR thickness of ~1.6 μ m. The sample is then soft-baked on a hot plate for 60 sec at 115 C degree. The next step exposes the sample to UV light using a contact mask aligner (Karl Suss MJB3 model) for 120 sec. Next the sample is developed using a MF-319 developer for 60 sec. For the lift off process (gold and aluminum), after the exposure step the side wall profile of the photoresist is sloping. This makes it difficult to strip the metal away during the lift off process. In order to make the metal lift off easier, the sample is dipped in a cholorobenzene solution for 60 sec and dried with nitrogen gas before being developed. This step causes the top layer of the photoresist to form an overhang profile of the photoresist side wall. This step helps the metal layer lift off easier [www].

The three other mask materials included titanium, silicon dioxide and silicon nitride. Patterns are formed in these materials with the same lithography procedure described above. A hard bake step using the hot plate at 120 C degree for 10 min before etching is done. For these three materials direct etching is done, instead of using a liff-off process as used for Al and Au. The silicon dioxide is wet etched with buffered oxide etch (BOE) and the titanium with an HF solution ($H_2O: H_2O_2: HF = 20:1:1$) [Will, 2003]. Two mask patterns used for the diamond etching studies are shown in Fig. 6. 12.

Figure 6.12.a shows a narrow pattern mask with the chevron lines ranging from 1 to 5 μ m in width and the etched trenches between them being equal in spacing. Figure 6.12 b shows the

wide pattern mask with serpentine lines. The etch trenches between the lines are 20 μ m width and the lines width are 5 μ m. So the lithography pattern feature sizes range from 1 to 20 μ m.



(a) Narrow mask (b) Wide mask



The five mask materials patterned on NCD diamond samples are shown in Figs. 6.13 through 6.17.



Figure 6.13: Aluminum mask on NCD sample (SEM image).



Figure 6.14: Gold mask on NCD sample (SEM image).



Figure 6.15: Ti mask on NCD sample (SEM image).



Figure 6.16: *SiO*₂ mask on NCD sample (SEM image).



Figure 6.17: Si₃N₄ mask on NCD sample (SEM image).

6.3.3.2 Effect of SF₆ on mask selectivity

Due to the micro-masking effect, whiskers often appear on the diamond surface after etching (with or without masking material) in pure oxygen plasma etching as described in section 6.3.4. The SF_6 gas is needed in the gas mixture in order to produce a smoother etched diamond surface. There are two factors that affect the selectivity, i.e. the diamond etch rate and the etch rate of the mask material. The addition of SF_6 to the etching process can change both the diamond etch rate and the mask material etch rate resulting in changes in the selectivity.

6.3.3.3 Selectivity results

The selectivity is determined for the various mask materials and for the etching plasma operating with and without SF_6 . In the first set of experiments, the diamond samples are etched with 2 sccm SF_6 added into the argon/oxygen plasma and in the second set of experiments, the diamond samples are etched with an argon/oxygen plasma only. The experiments are performed as shown in Fig. 6.18 where the cross-section of the pre-etch and post-etch samples a measured to determine the selectivity.



Figure 6.18: Dimensions used for Dektak and SEM to calculate the etch selectivity. Left figure is pre-etch cross-section and right figure is the post-etch cross-section.

The selectivity S_1 is determined from Dektak with dimensions as defined in Fig. 6.18 as

$$S_1 = \frac{C}{A - (B - C)}$$
 [6.3]

where

A: pre-etch mask thickness

B: post-etch step height

C: depth etched into the diamond

D: depth etched into the mask

E: post etch mask thickness

F: initial diamond thickness

G: the final diamond thickness

The second method to calculate selectivity S_2 is from SEM picture using dimensions as shown in Fig. 6.19

$$S_2 = \frac{C}{(A-E)} \tag{6.4}$$

We compared the two methods and the results are repeatable at \pm 20%.



Figure 6.19: Example of SEM method used to measure the etch selectivity. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm.

First we need to determine if there are any different selectivity results between the narrow and wide etch trenches. Both Dektak and SEM methods were used to calculate the selectivity for comparison purposes.

	Dektak		SEM	
Mask material and mask pattern	Narrow	Wide	Narrow	Wide
SiO ₂	4.5	2.1	4.6	3.2
Si_3N_4	5.7	4.5	4.0	4.0

Table 6.2: Mask selectivity comparison between narrow and wide pattern mask using both Dektak and SEM measurement methods. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm.

Mask material	Selectivity			
	SF ₆ (2 sccm)	No SF ₆		
Al	35	56		
Au	11	48		
Ti	1	12		
SiO ₂	5	8		
Si ₃ N ₄	5	7		

Table 6.3: Etch selectivity of five mask materials measuring using the Dektak profilometer. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:0-2$ sccm and a substrate location of z =-4 cm.

The results in Table 6.2 show that for the same masking material and etching condition, the selectivity of the wide mask pattern is slightly less than the selectivity of the narrow mask pattern. It is also be seen that both Dektak profilometer and SEM measurement results are not significantly different in terms of the selectivity value measured.

The selectivity results for all five materials are shown in Table 6.3. For this table, a third masking pattern with 4 μ m wide non-etched diamond lines separated by 4 μ m wide trenches (etched lines) was used as shown in Fig. 6.20.



Figure 6.20: Mask pattern transferred used for all mask materials to determine the selectivity (Optical image_500X).

Mask material	SF ₆ (sccm)	Diamond Etch	
		rates (nm/min)	
Al	0	189	
	2	121	
Au	0	120	
	2	32	
Ti	0	114	
	2	41	
SiO ₂	0	74	
	2	123	
Si ₃ N ₄	0	96	
	2	113	

Table 6.4: Comparison of NCD etching rates with and without SF_6 for different mask materials. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:0-2$ sccm and a substrate location of z =-4 cm.

It can be seen that the highest mask selectivity is 56 for an Al mask and the lowest mask selectivity is 1 for a Ti mask. The SF_6 gas also affected the mask selectivity. It can be seen that etching diamond with SF_6 degrades the selectivity for all masking materials. From Table 6.2, the

mask selectivity is higher without SF_6 compared with adding 2 sccm SF_6 . So by adding SF_6 into the argon/oxygen gas mixture to get rid of the whiskers, the mask selectivity decreases.

It is found that the change of etch rates caused by SF_6 depends on mask materials as shown in Table 6.4. The explanation for that contrast is the forming of fluorine compounds with the mask material; for example AlF₃ if using aluminum mask [Dors, 1995]. If the fluorine compound formed is nonvolatile, it acts like a micro-mask on the diamond surface so the diamond etching rate is decreased. In contrast, if the fluorine compound is volatile, the diamond etch rates is increased as shown in Table 6.4 for SiO_2 and Si_3N_4 .

So etching without SF_6 improves the selectivity of the hard mask but produces a roughness because of the whiskers that are formed randomly on the diamond etched surface.

6.3.3.4 Effect of DC bias on the selectivity

One of the important variables determining the selectivity is the substrate RF induced DC bias. In order to investigate the DC bias effect on the mask selectivity, five samples of NCD were prepared. An aluminum mask with a thickness of ~300 nm was deposited on the NCD samples with a size of 1.5 x 1.5 cm using the e beam evaporation method and then the samples were patterned. The etching recipe is keep the same with a power of 700 W, a pressure of 4 mTorr and a gas mixture of $Ar: O_2: SF_6 = 6: 20: 2$ sccm. The substrate bias was varied from

0 to -200 V. The ECR operation mode was used for this etching experiment. The Dektak method was used to determine the selectivity. The selectivity varied with the DC bias as shown in Fig. 6.21.



Figure 6.21: The etch selectivity versus the negative induced DC substrate bias. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, 0 to -200 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:20:0-2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

A more negative bias applied caused the mask selectivity to decrease. From section 6.3.1b the diamond etches rate increases when the negative bias increases. However, the mask (aluminum) etch rate increased more as compared with diamond etch rate. One of the possible explanations is that the increase of oxygen ions energy may retards the heterogeneous recombination of [F] atoms or reacts with aluminum fluoride (AlF_3) to liberate more fluorine atoms. So the [F] atoms increased will effect on the aluminum etch rate. The [F] ions energy increased when bias increased were also affected on the mask (Al) etch rate. Thus the selectivity is decreased when the negative DC bias increased.

6.3.4 Surface morphology

When etching NCD and MCD diamond with SF_6 in the feed gas, there are many whiskers appearing on the surface etched as shown in Fig. 6.22 b and d. The formation mechanism of whiskers when etching diamond with oxygen plasma is still unclear. They can be produced from micro-masking effects by the deposition of hard to etch materials onto the surface [Dors, 1995].

The typical spire like shape of whiskers on NCD surface after being etched 20 minute is shown in Fig. 6.23. The base diameter of spires is from 300 to 500 nm and the height is from 200 to 1,200 nm.









(c)

Original MCD surface

Etched MCD surface

(d)

(b)

Etched NCD surface

Figure 6.22: NCD and MCD etched surfaces. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:0$ sccm and a substrate location of z =-4 cm.



Figure 6.23: SEM image of the spire like shape of whiskers (UNCD etched surface without SF₆) The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:20:0-2$ sccm and a substrate location of z =-4 cm.



(a) Gold mask

(b) Ti mask



(c) Si₃N₄ mask







Figure 6.24: Comparison of whiskers formed on NCD diamond etched surfaces using different mask materials. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:20:0$ sccm and a substrate location of z =-4 cm.

The density of whiskers on the diamond etched surface is affected by the mask material as shown in Fig. 6.24. It can be seen that for the gold mask, the density of whiskers that appear on the etch surface is less than with other mask materials.



Figure 6.25: SCD surface etched without SF_6 _Al mask.

For etching of single crystal diamond without SF_6 , the formation of whiskers on the surface etched also occurs as shown in Fig. 6.25.





(b) MCD



(c) SCD

Figure 6.26: SEM image of the NCD and MCD etched surface with SF_6 added in the oxygen gas mixture. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm.

The addition of a small amount of SF_6 (2-3 sccm) in the oxygen plasma reduces or eliminates the formation of whiskers as shown in Fig. 6.26 a, b and c. The role of SF_6 gas in the mixture is to remove the micro masking formed on the etched surface.

Another phenomenon observed are random pits appearing on the SCD diamond etched surface as shown in Fig. 6.26 c. The distribution of these pits is not uniform and the density is range from 2- 7.6 x 10^8 pits/cm². These pits have been attributed to residual defects (mainly from dislocations) of SCD [Bern, 2004].

6.3.5 Surface roughness

Typically, the nature of plasma etching is using energetic ions to strike on the substrate. For the etching process, the physical sputtering is expected to make a rough surface after etching as shown in Fig. 6.27.



Figure 6.27: MCD etched surface (SEM image). The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and substrate location of z =-4 cm.



(a) (b)

Figure 6.28: Comparison between SCD pre-etch and etched surface (AFM image)

(a) Pre-etch surface, average surface roughness $R_a = 2.64 \text{ nm}$

(b) Etched surface, average surface roughness $R_a = 18.39$ nm

The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm.

Figure 6.28 shows the surface roughness R_a of SCD after etching is increase (about 16 nm as compared with the pre-etch surface).

In order to investigate the input variables affect on to the surface roughness, a series of five experiments are performed on NCD samples (1.5 x 1.5 cm squares and approximate NCD

Exp./Input	Power (W)	Pressure	Oxygen	SF ₆ (sccm)	DC Bias (V)
1 1			50	510(50011)	
		(mT)	(sccm)		
01	300	4	20	2	-185
02	500	6	10	4	170
02	300	0	18	4	-170
03	700	8	16	6	-162
04	900	4	20	2	-125
05	700	1	20	2	125
03	700	4	20	2	-123

thickness of 4 μ m). All five samples were processed with the same patterned as the mask material. The etching process input variables were changed as shown in Fig. 6.5.

Table 6.5: The series of experiment input variables

The output results including roughness and diamond etch rate are shown in Table 6.6. It can be seen that the surface roughness is improved with certain input variables as shown in Table 6.6. The smoothness improved about 13% at a removal rate of 1.36 μ m/ hr was achieved with etching condition as follows: a power of 700 W, a substrate bias of -162 V, a pressure of 8 mTorr and a gas flow rate of Ar: O_2 : $SF_6 = 6:16:6$ sccm.

Exp.Output	Original	Etched	R_a (nm)	Roughness	Rate (µm/hr)
	R_a (nm)	R_a (nm)			
01	3.18	4.17	0.99	Increase	3.333
02	4.65	4.36	-0.29	Decrease	1.59
03	5.84	5.08	-0.76	Decrease	1.36
04	5.99	7.67	1.68	Increase	10.04
05	3.19	3.97	0.78	Increase	7.29

Table 6.6: The etched surface smoothness results.

6.3.6 The radial uniformity

The radial uniformity of diamond etching is an important factor for micro-fabrication plasma processing. The uniformity of radial etching is affected by the plasma density uniformity distribution in the process chamber. The plasma shape for both ECR and non-ECR plasma were observed and discussed in Chapter 5. The radial etching uniformity for NCD using an ECR plasma shows in Fig. 6.29. It can be seen in the ECR plasma case, the etching rate have a high peak at a radius of 1 inch. The lowest etch rate is at the edge (at a radius of 3 inches). The uniformity for the ECR plasma used for diamond etching is around $\pm 6\%$.



Figure 6.29: The radial etching uniformity of diamond. The plasma etching condition included a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

By using the data of charge density and electron temperature for argon plasma as reported in Chapter 5 and using the empirical etching model as described above, an approximate of etch rate versus pressures for both magnet and non-magnet plasma operation modes as shown in Fig. 6.30.



Figure 6.30: The etch rate versus pressures model

Figure 6.31 shows the comparison between the theoretical model and experimental results for diamond etching rate versus pressures (ECR operation regime). The trend of both curves which the etch rates increase with pressures increased is very similar. The theoretical etching model plot will match with the experimental result which Y_i (the yield of CO molecules desorbed per ion incident on a fully covered surface) is ~1.05.



Figure 6.31: Comparison the etch rate versus pressures between theoretical model and experimental results. The plasma etching condition included a pressure of 4-45 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm. An aluminum mask was used.

Experiments have been performed to develop a diamond etching process for microstructure fabrication and to characterize the Lambda microwave plasma assisted etching system. Key etching results include:

- An anisotropic diamond plasma-assisted process has been developed that has nominal operating input parameters consisting of a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6$ = 6:20:2 sccm and a substrate location of z =-4 cm. This etching condition gives a etch rate of 6-10 µm/hr, a selectivity for an aluminum hard mask of 35, an anisotropic etching angle of 82 degree and an etch surface free of diamond whiskers or spires. This etch condition is compromise set of input settings for the plasma-assisted etching process that gives a good etch rate, high anisotropic etch profile, high selectivity and smooth post etching surface. Other observations from this etching process study include

- The etch rates increase with pressure and RF bias increases.

- The etch rates vary with the gas flow rates. The etch rates increase with oxygen flow rate increases but decreased with the SF_6 and Ar flow rate increases.

- The anisotropic angle decreases with the pressure increases.

- The highest mask selectivity is obtained with an Al mask (56) and the lowest mask selectivity is with a Ti mask (1).

- The mask selectivity decreases with the addition of SF_6 into the oxygen gas mixture.

- The whiskers density formed on the etched surface with gold as the mask material is less compared with other mask materials.

- The addition of a small amount of SF_6 (2-3 sccm) in the oxygen based plasma helps reduce or eliminate the formation of whiskers on the etched diamond surface.

- The non-ECR plasma produces a higher etch rate than the ECR plasma at the same etching condition.

- The radial etch uniformity varies over a diameter of 6 inches around \pm 6% for a pressure of 4 mTorr, a microwave power of 700 W, -125 V substrate bias, a constant gas mixture of $Ar: O_2: SF_6 = 6:20:2$ sccm and a substrate location of z =-4 cm.

- The etch pits on the SCD etched surface have a density that ranges from 2- 7.6 x 10^8 pits/cm².

CHAPTER 7

DIAMOND SMOOTHING

7.1 Introduction:

Microcrystalline diamond (MCD) films are used for many applications like coating tools, diaphragm coating, heat sink, SAW filters, X-ray windows or other advanced devices [Chun, 2001]. Due to the columnar growth nature of MCD, the diamond surface is very rough, especially for thick diamond films [Grae, 1992]. Surface reflection for optical windows, non reproducible electrical contact, and insufficient thermal contact are some limitations for non-smooth MCD surface. Polishing of diamond is a difficult task since it is the hardest material and inert to most chemical substances. Polishing or planarization techniques are needed to smooth the MCD surface roughness to a specific requirement for various applications at a low cost.

The traditional mechanical lapping to smooth MCD diamond films is a well-known method in the industry but very challenging due to extremely slow diamond removal rates [Mals, 1999]. Therefore this method is not cost effective and it is time consuming. Several polishing technologies have been reported in literature for reducing the surface roughness of MCD diamond films. Those techniques include chemical mechanical polishing [Gril,2000], chemical polishing [John, 1994], thermal chemical polishing [Yosh, 1990], laser polishing [Ozka, 1997] and ECR air plasma etching [Herm, 1996]. Choosing a proper polishing technique for diamond smoothing is an important task that needs to be based on the application requirement and

economic constraints. In this chapter, techniques discussed in the research literature to smooth diamond surface are reviewed. Next methods to polish the microcrystalline film using plasma etching combined with mechanical polishing and planarization are developed. Finally, the results of diamond polishing using these techniques are reported.

7.2 Diamond smoothing mechanisms overview

This section describes the basic mechanisms of various diamond smoothing techniques. There are different ways to reduce the surface roughness of microcrystalline diamond films. The diamond smoothing techniques are: 1) Micro-chipping; 2) Phase transformation of diamond to graphite combined with micro-chipping method; 3) Atomic diffusion method; 4) Evaporating/Ablating; 5) Sputtering/etching; and 6) Chemical reactions [Mals, 1999].

The temperature factor is the critical condition for most of the diamond smoothing techniques except for the micro-chipping mechanism.

7.2.1 Micro-chipping:

This method uses the friction force between two moving surfaces in contact and its rate depends on the rotation speed and pressure for diamond smoothing. When the friction force is higher than the atomic binding energy of diamond, the carbon atoms on the surface layer are deformed or chipped away depending on the brittleness of the material [Bhus, 1991]. The removal rates depend on the friction force and in general soft materials are removed faster than hard materials. In diamond polishing, the micro-chipping process is used in mechanical lapping/polishing. The roughness and removal rate are related to the size of the abrasive powder used. The coarse powders are used for lapping and the fine powders are used for polishing. In micro-chipping processes, the contact area increases with lapping/polishing time. Consequently, the shear force per unit contact area decreases and the material removal rate decreases. So, in order to maintain a constant removal rate, the contact force must be increased as a function of time to accommodate the increase in contact area. This mechanism occurs in mechanical and chemo-mechanical polishing techniques.

7.2.2 Phase transformation of diamond to graphite or non-diamond carbon, and then removed by micro-chipping:

Graphite is one of the four allotropes of carbon including graphite, diamond, amorphous and lonsdaleite [Spea, 1989]. Graphite is the only one in the group that has a stable structure under atmospheric conditions. Other lattice structures are metastable. The two most well know allotropes are graphite and diamond. The graphite lattice is formed from trigonally bonded sp^2 hybridized carbon atoms and diamond lattice is formed from tetrahedrally bonded sp^3 carbon atoms. In diamond, the four equivalent sp^3 bonds form strong bonds that are very hard to remove. Graphite, on the other hand, has a weak bonding between the planes that are bonded by Van der Waals forces, and hence it is removed easier by mechanical polishing. Due to the diamond lattice structure being metastable, it can be transformed into graphite if enough activation energy for phase transformation is supplied [Mals, 1999]. When diamond is in contact with some catalytic materials such as iron, cobalt and nickel at 750 0C , it starts changing its lattice structure and transforms into graphite or other non-diamond carbon [Pier, 1993].

Hence the parts of the diamond crystal that come into contact with a catalytic material are changed to graphite and then the graphite can be easily removed by mechanical polishing because of weaker of binding forces. The process can be repeated until the surface is smooth. This mechanism plays a significant role in some polishing techniques such as thermal chemical polishing and dynamic friction polishing.

7.2.3 Diffusing carbon atoms into soluble metals:

Some soluble metals such as iron (Fe), nickel (Ni), manganese (Mn) and rare earth alloys (molybdenum, cerium and lanthanum) can react with any source of free carbon and absorb it into their surface. Such a reaction is easily triggered under certain temperature and pressure conditions occurring in the mechanical lapping/polishing process. When a diamond surface comes into contact with a metal disk at a temperature from 730- 1000 ⁰ C, carbon atoms in diamond diffuse into the metal disk until it is saturated [Hark, 1990] [Rame, 1997]. This process is called the metal hot plate polishing process. The diffusion rate of carbon atoms from protruding regions of the carbon substrate is greater than other regions due to a shorter diffusion path. Thus after polishing by this technique, the protruding regions of the diamond will be removed and the diamond surface ends up smoother. The carbon concentration of a soluble metal in contact with diamond depends on the distance from the interface, the diffusion coefficient and is given as following [Mals, 1999]:

$$C(x) = C_1 \left[erfc\left(\frac{x}{2\sqrt{Dt}}\right) \right]$$
[7.1]

where C(x) is the concentration at x; C_1 is the interface concentration; erfc is the error function; x is the distance from the interface; D is the diffusion coefficient; and t is time. This means when the carbon diffusion coefficient and the carbon solubility of the mating material increases, the removal rate increases. A thin piece of metal accommodates less carbon atoms than a thick piece, so a thin piece is saturated more quickly.

A hydrogen atmosphere can also be used in the metal hot plate polishing diamond method. With hydrogen present in the process the carbon atoms that diffuse into the metal surface react with hydrogen forming methane gas, which is carried away. The metal will not saturate with carbon atoms in this case and the removal rate is higher. The diamond removal rate with a hot metal plate contact method is also higher in vacuum than in hydrogen atmosphere. Because in the vacuum, the diamond film contacts closely with an iron plate and the carbon can diffuse rapidly [Toku, 1992].

7.2.4 Evaporation/Ablating:

If effective heat sources like torches, electric arcs or lasers are applied to the protruding crystal on the surface of diamond film, they will evaporate to produce a smooth surface. For example a laser beam is a suitable source for evaporating diamond film because it's a high density heat source that can be easily controlled. The short energy pulse generated by laser beams creates a localized heat region and the heat does not spread widely to the other parts of the diamond substrate. By adjusting the incident angle of the laser light to focus the energy into the protruding portions of the diamond substrate, it will generate a flatter surface [Tosi, 1995].
7.2.5 Sputtering:

Diamond can be removed using a sputtering process in which highly energetic ions collide with diamond on the surface and break its bonds. The carbon atoms are detached from the diamond surface. The ion source must be stable and a uniform density of the ion beam is needed to produce a good finish. The sputtering rate can be controlled by changing the ion energies and densities. The sputtering rate also depends on the amount of graphite contained in diamond sample. If there is more graphite in MCD diamond, the sputtering rate is higher, since the sputtering rate of graphite is higher than diamond [Bach, 1993].

7.2.6 Chemical reaction:

Diamond is extremely chemical inert and it does not reacted with any acids except at high temperature at which the acids can act as oxidizers to diamond. Two oxidizing reagents: KOH and KNO_3 will react and etch diamond at elevated temperatures. The temperatures should be slightly above the melting temperatures of potassium hydroxide (KOH) and potassium nitrate (KNO_3), which are 360° C and 324° C respectively [Olli, 1999]. The heat energy decomposes the liquid into oxygen and other constituents near the diamond surface. The oxygen generated reacts with the diamond on the surface and forms the volatile gases CO and CO_2 . This reaction is used in chemo-mechanical polishing. In other reactions, diamond will be oxygenated before graphitized in contact with oxy-acid such as H_3PO_4 and $NaNO_3$.

Diamond can react with elemental metals such as tungsten, tantalum, titanium and zirconium to form carbides, hence they can act as solvents. Diamond can also be etched when it is exposed to a reactive atmosphere, such as oxygen or hydrogen at elevated temperatures. Carbons atoms in diamond are converted into CO_X or CH_X gas. These chemical reactions are involved in most polishing techniques such as thermal chemical polishing, chemo-mechanical polishing and dynamic friction polishing.

7.2.7 Summary:

This section summarizes the diamond smoothing mechanisms. Each diamond polishing technique involves one or more different diamond smoothing mechanisms. Diamond can be polished directly (path 1) or indirectly through two or more steps (path 2-5) by using different polishing mechanism as shown in Fig. 7.1.



Figure 7.1: Diamond polishing mechanism diagram

- Path 1 Fig. 7.1 shows diamond polishing directly via micro-chipping by mechanical, evaporation, ion beam or laser polishing.
- Path 2 in Fig. 7.1 shows diamond can be polished indirectly by converted it into graphite under high temperature and pressure without contact with soluble metals, and then removed from the surface by micro-chipping, or chemical reactions with gas to form CO_X , carbides or CH_X . The graphite is also removed by atomic diffusion into metal.
- Path 3 shows diamond can have a surface reaction with different reactive gases such as oxygen or hydrogen to form CO_x or CH_x , respectively. In thermal chemical or dynamic friction polishing method, the reactive gas like oxygen or hydrogen acts as an agent, removing the graphite formed on the polished diamond surface. The oxygen gas can also oxidize a metal such as iron to form iron oxide (Fe_2O_3). This oxide will react with carbon to form a volatile CO_x gas, reducing the carbon level in a metal disk. The metal will then have more room to absorb the carbon from the diamond surface.
- Path 4 shows that carbon atoms from protruding regions of a diamond surface in contact with a soluble metal surface can be diffused into that metal surface under certain temperatures and pressure. Some oxidizing agents such as potassium nitrate (*KNO*₃) or potassium hydroxide (KOH) can etch diamond at lower temperatures through a oxidation process.
- Diamond can also be smooth directly using a RIE plasma or ion beam etching technique by combining the etching technique with a sacrificial layer such as gold (Au), photo resist, silicon nitride (Si_3O_4) or silicon dioxide (SiO_2). A sacrificial layer covers the diamond surface except for the protrude portions. Then the diamond exposed parts are

removed by plasma etching. The process can be repeated multiple times until the surface is smooth. This method can also be combined with mechanical polishing for a smoother surface result (R_a less than 100 nm). Compared to other methods, this method has good potential for practical application, especially for thick MCD diamond films which have very rough surfaces.

7.3 Techniques used to polish diamond film:

7.3.1 Mechanical polishing:

The traditional mechanical lapping has been used to smooth diamond surfaces for a long time. Detail of this method can be found in the literature [Fiel, 2001] [Hird, 2002].

This method involves simple abrasion of rough diamond surfaces using a suitable abrasive like diamond powder. The lapping proceeds by grinding the diamond sample on a cast iron rotating wheel (called a scaife) rotating at a high speed. The abrasive is in the form of slurry of powder and liquid. Diamond powder is mixed with olive oil, ethylene glycol or some other base to form a paste or suspension which is rubbed over the metal scaife and then left for some time for the suspension to be absorbed by the pores. The surface of diamond to be polished is placed against the scaife typically about 300 mm diameter rotating at 2500 rpm under a load of the order of 1 kg. A contact pressure of 2.5-6.5 MPa applied for diamond lapping and 2.5 MPa applied for polishing process are recommended by Ralchenko [Ralc, 1998].The final surface finish is controlled by the size of the abrasive powder used. A coarse powder up to 50 µm is used in the initial stage of polishing, which allows for faster material removal rate. A sequence of

polishing steps with smaller diamond particle sizes can be used to obtain the desired smoothing surface. When the diamond particle size decreases, the removal rate is also decreased. Mechanical polishing is usually used for polishing single crystal diamond. For MCD, the mechanical polishing method works a slower removal rate because of the randomness of crystal orientations. The removal rates for the (100), (110) and (111) planes are in the ratio 0.6:1:0.1 (the wheel speed is 2932 rpm and load is 2015 g) [Wilk, 1991]. A schematic of mechanical lapping system is shown in Figure 7.2. Polishing rates depend on the type of abrasive used, the rotating wheel speed and the crystal orientation being polished [Hick, 1991]. This traditional diamond smoothing method is often not cost effective due to the polishing rate for MCD being slow.



Figure 7.2: Mechanical polishing schematic

From the literature, there are three wear mechanisms of mechanical polishing [Grill, 1997]:

- Chemical wear: The transformation of diamond to graphite or other non diamond carbon on the surface of the diamond while it is being polished. And then the material is detached from the surface because of the weaker bonding structure of graphite.
- 2) Thermal wear: Burning or carbonization takes place because of the temperature rise at individual hot spots due to friction force. The high temperature modifies the mechanical properties of the diamond enhancing the mechanical component of wear.
- Electrical wear: An attractive force due to tribo-charging has been observed for diamond sliding on a rotating surface of amorphous carbon. Although sparking may occur during polishing, it is believed not to cause material removal [Gril, 1995].

Experimental data of mechanical polishing of MCD diamond is shown in Fig. 7.3. It took 60 hours to reduce the surface roughness from 1700 nm to ~150 nm.



Figure 7.3: Experimental mechanical polishing [Loew, 2009]. The five data sets (#1, #2, #3, #4 and center) are different locations on a 1 inch diameter MCD film polished on a Logitech polisher

7.3.2 Thermal–Chemical (Hot-Metal plate) polishing:

Thermal chemical polishing is based on the atomic dissolution of carbon into a hot metal plate. The soluble metal plate (made of iron or low carbon steel (0.2% C or lower), nickel, manganese, molybdenum, etc.) is heated to 950 C and abrades against the diamond film in the

presence of an argon or hydrogen atmosphere [Toku, 1991]. The plate surface is smoothed to an approximated roughness of 2 μ m using a grinding technique. The scaife is usually loaded with a weigh to create a pressure of 20 kPa. A schematic of thermal polishing of diamond is shown in Figure 7.4 [Mcco, 1994). The diffusion of carbon from a diamond surface into metal results in the formation of a carbide layer on the surface which is removed easily using HCl acid.



Figure 7.4: Thermal polishing of diamond schematic [Mcco, 1994].

The polishing rate depends on the diffusion of carbon atoms from the diamond surface into the hot metal plate. The thermal chemical polishing rate is higher in vacuum but the surface is smoother in a hydrogen atmosphere [Mals, 1999]. The temperature of the metal hot plate is also important for the polishing rate. The range of temperature for this technique is from 730-950 ${}^{0}C$ [Toku, 1991]. Polishing is not very efficient at lower temperatures because of less chemical reactivity. The diamond removal rate can be increased by controlling the temperature to be greater than the melting point of the metal carbide and less than the melting point of the metal itself [Tzen, 2000]. The metal carbide melts around the points of contact between the diamond and the metal surface. This process accelerates the diffusion of the diamond into metal. Therefore the diamond removal rate is increased. When the diamond surface is smooth, it is cooled and cleaned with HCl acid to remove metal carbide residues.

7.3.3 Chemically assisted mechanical polishing (CAMP):

The CAMP technique combines mechanical polishing and oxidizing reagents such as *KOH*, *KNO*₃, or *NaNO*₃ to enhance the diamond removal rate. This method exploits the high temperature oxidation property of diamond [Olli, 1999]. Diamond under an applied load, in contact with a base plate (made of alumina or cast iron), that is rotated and covered with *KNO*₃ is shown in Fig. 7.5 [Wang, 2006]. Diamond abrasive powder can be used to assist the mechanical polishing process to increase the diamond removal rate. The diamond polishing rate directly depends on the speed of the wheel and the applied load (weight).

In order to increase the removal rate and lower the operation temperature, a mix of oxidizing agents such as potassium permanganate and sulfuric acid ($KMnO_4 + H_2SO_4$) has been used in the polishing process [Chen, 2005]. The advantage of this technique is it can polish a non- planar diamond film. Moreover, the damage after CAMP polishing is much less than mechanical polishing [Hsie, 2002].



Figure 7.5: The CAMP polishing schematic [Wang, 2006]

In the CAMP polishing technique, the compound effect of mechanical abrading and oxidant plays an important role in the polishing rate. During polishing the protruding portions of the MCD diamond surface contacts with the diamond powder on the surface of the metal disk, which can generate micro-cracks on the diamond surface. The oxidizing chemicals enter the micro-cracks and react with diamond to form CO_2 and CO under elevated temperature and pressure conditions. So the carbon atoms from diamond surface are diffused into the oxidizing agents. Therefore, a higher removal rate than conventional mechanical polishing is obtained.

7.3.4 Laser polishing:

Laser energy can be used to smooth diamond without physically contacting the diamond. This technique is applied for the smoothing of very thin MCD diamond film which would be easily broken by other techniques that apply pressure or force to the surface. This technique is also applied on non-planar shapes or localized regions of diamond films. The diamond is irradiated with a pulse laser at a repetition rate from 1 to 100 Hz. A schematic of laser polishing technique is shown in Fig. 7.6.



Figure 7.6: Laser polishing schematic [Bhus, 1994]

7.3.5 Dynamic friction polishing (DFP):

The DFP polishing method was developed from a thermal chemical technique [Suzu, 2003]. A MCD diamond film is polished at a predetermined pressure by a metal disk without abrasive powder. The metal disk is rotated at a high speed in the atmosphere. This polishing method generates dynamic friction between diamond and the high speed metal disk. The DFP polishing method also enables a highly efficient thermal chemical reaction induced to smooth

diamond surface. A schematic of the dynamic friction polishing system is shown in Fig. 7.7 [Iwai, 2004].



Figure 7.7: Schematic of dynamic friction polishing [Iwai, 2004].

7.3.6 Electrical discharge machining (EDM)

Electrical discharge machining (EDM) is a polishing method using the thermal energy produced by a pulse spark discharge to erode the MCD diamond surface. A spark discharge generates a high energy density at high temperature that can melt and evaporate a local region of the diamond film. The gap between the electrode and diamond work piece is filled with a dielectric fluid, typically either deionizer water or hydrocarbon oil. This confines the effect of the spark discharge to a small area, dissipates heat from the eroded surface and flushes away the debris [Olse, 2004]. For the non-conductive MCD diamond film, the film usually is coated with a thin layer of electrically conductive material before polishing. The peaks of the MCD diamond are removed quickly during the EDM process. The EDM polishing mechanisms are as follows: explosion caused by the spark, graphitization of diamond, evaporation and oxidation of carbon and chemical reactions to form carbides [Guo, 2002]. EDM is suitable for rough polishing with a high polishing rate at3 μ m/min. It should be combined with other polishing method to achieve a required smooth surface if the final surface roughness is less than 1 μ m. A diagram of the EDM polishing technique is shown in Fig. 7.8



Figure 7.8: Schematic of EDM polishing [Guo, 2004].

7.4 MCD diamond planarization and polishing using a plasma etcher:

7.4.1 Introduction:

Plasma etching is a key technique for diamond post processing. Plasma etching is able to remove diamond effectively across large areas in a controllable manner. Plasma etching also can be used on non-planar surfaces of diamond thin films at a low processing temperature, which is something other methods are not be able to achieve. Plasma etching naturally cannot reduce the surface roughness of MCD diamond films because it removes the diamond not only on the protruding portion of the film but also on the whole surface of diamond. So the surface roughness overall is not improved. The important factor to plasma etching is to restrict the etching to only the protruding portions or the peaks of diamond films. This way the diamond film will be smoother after the polishing process. Some planarization methods using plasma etching are reported in literature and they were reviewed in detail in Chapter 2.

This section will report the various planarization techniques developed to smooth diamond using plasma etching combine with mechanical lapping and masking layers. The surface roughness is characterized using a Dektak profilometer model D6M as described in Chapter 3. The surface roughness measurements include the average roughness (R_a) and the ten point height average (R_z). The average roughness R_a is the arithmetic average deviation from the mean line within the assessment length L and is defined by the equation [Dektak 6M Manual, 2002]:

$$R_a = \frac{1}{L} \int_{0}^{L} |y| dx$$

where L is the scan length.

The R_z value is defined as the difference in the height between the highest peaks and the lowest valleys relative to the mean line.

$$R_{z} = \frac{1}{5} \left(\sum_{i=1}^{5} Y_{pi} + \sum_{i=1}^{5} Y_{vi} \right)$$

where Y_{pi} is the highest peak at point i and Y_{vi} is the lowest valleys at point i.

Most of the polishing experiments in this research are multiple step processes and the surface roughness in each step is measured using the Dektak profilometer. The following sections discuss three planarization techniques.

7.4.2 Photo-resist reflow method:

This planarization technique uses photoresist Shipley 1813 and silicon nitride (Si_3N_4) as a sacrificial layer to coat over the MCD diamond surface. The purpose of the layers are to control the plasma etch to occur only on the protruding portions of the diamond film. This planarization process is described as follows. A layer of Si₃N₄ film with a thickness of 1 µm is deposited on the diamond substrate by a PECVD system. After that, a layer of photo resist, Shipley 1813, with thickness of 1.6 µm is spun on the top of the Si_3N_4 layer. Next, the sample is heated up to 150° C. The photo resist is melted and it flows on the substrate. It will cover the dips or valleys and not the exposed or the protruding regions to be etched. The Si₃N₄ layer that covers the MCD diamond is etched using a SF₆ plasma (gas mixture of Ar:SF₆ = 10:4 sccm) for 10 min. This etching process exposes the high tips or regions of the diamond. After that the exposed diamond is etched using an ECR oxygen plasma (gas mixture of $Ar:O_2:SF_6 = 6:20:2$ sccm) for 1 hour. The process is repeated until the surface roughness is not further improvable as shown in Fig. 7.9.



Figure 7.9: Diagram of Photoresist Reflow Method.

- (a) The original MCD diamond surface.
- (b) Surface formed by depositing Si_3N_4 (~1µm thick) followed by photoresist (PR) 1813 (1.6 thick) on top of the Si_3N_4 layer. Then the PR is reflowed at 150 C degree follow by a Si_3N_4 plasma etched.
- (c) Plasma etch surface to get rid of the crystal peak of diamond.
- (d) Repeat steps a through c until the MCD surface is smooth.

Figure 7.10 shows the optical images of photoresist reflow method processing. Figure 7.10 (a) shows the original microcrystalline diamond surface is very rough. Figure 7.10 (b) shows the surface after being masked with Shipley 1813 photo resist on the top of Si_3N_4 and microcrystalline diamond substrate. The sharp crystal tips of the MCD diamond are exposed and ready to be etched. Figure 7.10 (c) shows the surface after being etched 1 hr. The figure shows all the sharp peaks of the MCD are etched away. Figure 7.10 (d) shows the surface after it is cleaned and ready for the next masking step. Figure 7.10 (e) shows the MCD diamond surface after being etched 5 steps and the sharp crystal tips are almost gone. The surface is much smoother as compared with the original surface.



(a)

(b)



(c)

(d)



(e)

Figure 7.10: Smoothing microcrystalline diamond process (Optical images _500X)

- (a) Original microcrystalline surface;
- (b) Pre-etch surface preparation (Si_3N_4 and photo resist Shipley 1813 masking layer on the top of microcrystalline diamond surface)
- (c) Etched surface (etching time: 1 hr)
- (d) Etched surface without Si_3N_4 and photoresist (etching time: 1 hr)
- (e) Etched surface without Si_3N_4 and photoresist (etching time: 5 hrs)



Figure 7.11: The peak height of crystals (R_z) versus etching time. C is the center location and E is the edge position.

The average peak height of the MCD film (R_z) is reduced from 14 µm to around 1 µm as shown in Fig. 7.11 (measured from the Dektak). The surface roughness R_a of the MCD diamond film is also greatly improved after 5 steps as shown in Fig. 7.12. The R_a is reduced from 1.8 µm to around 300-600 nm. The total time for this process is ~7 hrs.



Figure 7.12: The surface roughness (R_a) versus etching time. $R_a(C)$ is at the center of the sample and $R_a(E)$ is near the edge of the sample. The sample size was 02 inches diameter.

The polishing rate is the difference between the original surface roughness R_a (original) and the final surface roughness R_a (final) over the total time of the polishing process. The average of the smoothing rate for the photoresist reflow method is ~170 nm/hr. The advantage of this polishing method is to reduce the time consumed to smooth the surface as compared with other methods like mechanical lapping (~10 nm/hr). A limitation of this method is the surface roughness cannot be reduced down to the nanometer range. A different lapping/polishing method needs to be involved after this process achieves a R_a of ~500 nm in order to get the surface roughness smooth to a few tens of nanometer scale.

7.4.3 The plasma roughing of the surface combined with mechanical polishing method



(a)

(b)

Figure 7.13: The surface morphology of micro-crystalline diamond. (a) pre-etch and (b) after etched using oxygen plasma etching (SEM images). Pressure of 4 mTorr, a microwave power of 700 W, -125 VDC induced substrate bias, and a gas mixture $Ar:O_2: SF_6 = 6:20:0$ sccm.

The second method uses plasma etching combined with mechanical polishing to smooth micro crystalline diamond. Fig 7.13 shows the effect of oxygen plasma etching on MCD diamond. The grass like structure or whiskers that appear on the MCD diamond surface after

etching with oxygen plasma are easily removed by the mechanical polishing in this method. The plasma roughing of surface for mechanical polishing process is shown in Fig. 7.14.



Figure 7.14: Plasma roughing of surface for mechanical polishing process.

- (a) MCD original surface
- (b) Plasma etch diamond
- (c) Lap/polish diamond surface
- (d) Repeat step a-c until the diamond surface is smooth.

The result of using plasma etching combine with mechanical polishing is shown in Fig. 7.15. The process uses a plasma etching pre-treatment of the MCD diamond substrate for 10-15 minutes followed by lapping for 1hr. The etching and lapping processes are repeated 5 times. The surface roughness R_a improves from 1048 nm to 290 nm in roughly six hours and 20 minute. So the polishing rate is about 120 nm/hr.



Figure 7.15: The surface roughness versus process steps for MCD sample KWH 35. The plasma conditions include pressure of 4 mTorr, microwave power of 700 W, -125 V substrate bias and gas mixture $Ar: O_2: SF_6 = 6:20:0$ sccm.

Figure 7.16 shows the result of polishing MCD versus lapping time using the plasma enhance mechanical polishing method for sample KWH 36 that started with a surface roughness

 R_a of 3802 nm. The etching time for each surface pre-treatment is keep constant at 20 minutes. The surface roughness is reduced from 3802 nm down to 53 nm in 23 hrs. So the smoothing rate is approximately 120 nm/ hr. The plasma etching is not used for the surface roughness reduction with R_a less than 53 nm, rather mechanical polishing only is used.



Figure 7.16: The surface roughness R_a versus lapping time for MCD sample KWH 36. The plasma conditions include pressure of 4 mTorr, microwave power of 700 W, -125 V substrate bias and gas mixture $Ar: O_2: SF_6 = 6:20:0$ sccm.

7.4.4 Plasma-assisted etching with selectivity of one:

A. *SiO*₂/Diamond:

This planarization method combines a sacrifice mask (SiO_2_PECVD), mechanical lapping/polishing and plasma-assisted etching. The idea is to start by depositing SiO_2 on the diamond surface with a PECVD system as described in Chapter 3. The deposition parameters used include a pressure of 1000 mTorr, a power of 20 W, a gas mixture of $N_2O:SiH_4 =$ 710:170 sccm and $300^{\circ}C$ substrate temperature. Mechanical lapping is used in the next step to planarize the surface as shown in Fig 7.18. The protruding portions of the SiO_2 sacrifice layer will be easily removed by the mechanical lapping to produce a smooth flat surface. The key aspect of this method is to use a recipe for the plasma etching which etches both diamond and the sacrifice mask layer with the same etch rate, i.e a selectivity of one. This step removes the sacrifice layer and protruding portions of diamond at the same rate. The process can be repeated until the diamond surface roughness decreases to the desired smoothness.

A series of experiments are performed to determine the ratio of the etching rate between SiO_2 and diamond. An oxygen plasma is key to etching diamond and an SF_6 plasma is used to etch SiO_2 . So a mixture gas of O_2/SF_6 is used to get an etching selectivity of one. For the first experiment, NCD is used because they have smooth surfaces and hence it is easy to determine the selectivity. Sample NCD # 57 was cut into 0.5 x 0.5 inches and pre-cleaned using the RCA cleaning process. The samples are then deposited with a layer of 2.7 µm thick SiO_2 . The SiO_2

was patterned and plasma etching using different feed gas mixtures. The recipe of the plasma etching was kept the same except for SF_6 gas flow which varied from 2-10 sccm.



Figure 7.17: The selectivity of NCD and SiO_2 . The plasma etching condition included a pressure of 4 mTorr, a power of 700 W, substrate bias of -125 V, a gas mixture of Ar : O_2 = 6:20 sccm, a SF_6 flow rate of 2-10 sccm and an etching time of 20 min.

Dektak measurements determined the selectivity. Figure 7.17 shows the selectivity of NCD diamond and SiO_2 for varied flow rates of SF_6 . The experiment parameters are

microwave power of 700 W, a substrate bias of 125 V and pressure of 4 mTorr. The results in Fig. 7.17 show that the selectivity is 1 at a SF_6 flow rate of 4 sccm. The next experiments were done using on MCD diamond with the recipe kept the same as for NCD diamond with the exception that the substrate bias was varied. A selectivity of 1.07 (MCD/ SiO_2) was achieved for etching parameter as follows: a pressure of 4 mTorr, a microwave power of 700 W, a substrate bias of -190 VDC and a gas mixture Ar: $O_2: SF_6$ of 6:20: 4 sccm.

The detailed steps for the selective of one process to smooth MCD diamond films are:

- Fill the microcrystalline diamond surface (Fig. 7.18 a) with the SiO₂ layer (spin-on-glass (SOG) or PECVD) as shown Fig. 7.18 b. The thickness of coating layer depends on the diamond roughness.
- 2. Lap for 15 min to get the surface smooth and planar as shown Fig. 7.18 c
- Use plasma etching (1 hr) with parameters set to give a selectivity of one for SiO₂ on diamond.
- 4. Repeat steps 1, 2 and 3 until the roughness of diamond surface is as smooth as possible (Figure 7.18 d).



Figure 7.18: The selectivity of one diamond smoothing process.

One sample used for this polishing method was sample GYJ 21. The initial measurements of sample MCD diamond number GYJ 021 was a thickness of 252 μ m, a surface roughness R_a of 4.636 μ m and an average R_z of 27.377 μ m. The original surface of sample GYJ 021 is very rough as shown in Fig 7.19a. First a 30 μ m layer of oxide SiO_2 was deposited using the PECVD system as described in Chapter 2. Figure 7.19 b shows the surface of sample GYJ 21 after deposition of the SiO_2 layer. Figure 7.19 c shows the surface of sample GYJ 21 after used mechanical lapping for 15 min. The sample was then etched by the ECR plasma etcher for 1 hr with a selectivity recipe as described in previous section. Figure 7.19 d show the surface of sample GYJ 21 after the first cycle of plasma etching. The average surface roughness R_a after one cycle is significant reduced from 4.861 μ m down to 0.902 μ m. The polishing process is repeated five cycle steps and the final surface roughness is reduced to 140 nm as shown in Fig. 7.19 e.



(b)



(c)

(d)



(e)

Figure 7.19: Optical images 500 X of polishing process by selectivity of 1 method (sample GYJ 21)

- a. The original MCD surface
- b. The MCD surface after deposited SiO_2 layer
- c. The surface after mechanical polishing
- d. The MCD surface after plasma etching
- e. The final result of polishing process (after five process cycles)



Figure 7.20: The surface roughness versus processing cycles.

Figure 7.20 shows the surface roughness reduced after each polishing process cycle. The total time for this process is 25.5 hrs. The average smoothing rate for this polishing process is 185 nm/hr.

B. SOG/Diamond:

Spin on glass (SOG) is a type of glass that can be applied as a liquid and cured to form a layer of glass having characteristic similar to those of SiO_2 . SOG has been used for planarization on diamond as reported by Chakraborty [Chak, 1995]. SOG model Acculass T 512 B is used for the experiments. The SOG coating on diamond process is as follows. The SOG is warmed up to room temperature for 30 minutes. Then the SOG is heated up to 80 C degree for 1 minute. The SOG is applied to the diamond sample by spin coating at 3000 rpm for 30 seconds followed by a soft bake at 80 C degree for 1 minute. The next step is baking the sample at 150 C degree for 1 minute followed by a hard bake at 250 C for 1 minute. The last step is curing the sample using a thermal furnace at 425 C degree for 1 hour using nitrogen gas flow.

Layers	R_a (Original)	R_a (SOG)	<i>Rz</i> (Original)	Rz (SOG)
	(nm)	(nm)	(nm)	(nm)
03	475.9	295.7	3131.8	1886.9
05	475.17	243.06	3222.7	1659.2
07	485.22	240.7	4067.3	1385.1

Table 7.1: Multi-layers coating of SOF surface roughness on silicon (unpolished side)

A single layer of SOG coated on MCD diamond is very thin (less than 500 nm if applied with a 3000 rpm spin speed) [see Acculass T512 B manual). To increase the thickness, some initial experiments of coating multiple SOG layers was done and then examined to see if any cracking of the surface occurred. The first series of test were performed on silicon (unpolished side). For less than seven layers of coating, the surface roughness improved as shown in Table 7.1. Both the surface roughness R_a and the average peak R_z are reduced after being coated from three to seven layers.

In order study the planarization of this polishing method, two layers of the SOG are coated on a MCD diamond surface. Using the Dektak profilometer to measure the surface roughness, the surface roughness is reduced from 53.12 nm to 12.61 nm. The plasma etch selectivity of the SOG coating on NCD diamond also was observed. Two NCD samples with the same growth conditions were used to determine plasma etch condition when the selectivity is one. The two samples were coated with two layers of SOG and treated with the same process as described above. The two samples then were etched with the same conditions except for variation the SF_6 gas flow rate. The etching conditions included a power of 700 W, a pressure of 4 mTorr and a substrate bias of -125 V. The selectivity of SOG and NCD diamond is 0.985 with the SF_6 gas flow rate at 3 sccm as shown in Table 7.2.

Sample	Ar: O_2 : SF_6 (sccm)	Selectivity
NCD_DT01	6:20:4	0.81
NCD_DT02	6:20:3	0.985

Table 7.2: The selectivity of SOG versus SF_6

The planarization using SOG method was not successful to reduce the surface roughness for the MCD diamond film with a surface roughness R_a larger than 2 µm because the MCD surface is rough and need a thick SOG to cover the whole surface. The multi-layers SOG coating is limited due to the cracked SOG surface occur when process on a MCD diamond with a roughness R_a larger than 2 µm.

7.5 Summary

- Polishing of a MCD diamond is a complicated process due to the extreme hardness of diamond material. This chapter overviews the theory of polishing mechanisms and develops effective plasma-assisted polishing techniques to obtain a smooth diamond surface in less time.

Three methods of diamond smoothing are investigated including: 1) photoresist reflow method;2) plasma roughing of surface for mechanical polishing; and 3) Etching with selectivity of one.

- All three polishing methods utilized the plasma-assisted etching process as a key step to remove the protruding regions of diamond surface to reduce the surface roughness of the MCD diamond.

- Three methods to smooth thick MCD diamond substrates were investigated using microwave plasma etching combined with mechanical lapping/polishing and sacrificial layers.

- The method of forming a hard mask in the valleys of the MCD surface using a photoresist reflow technique worked well for removing the larger protrusions (> 500nm) from the surface.

- The method of plasma etching with selectivity of 1 combined with mechanical lapping/polishing of a sacrificial SiO_2 layer quickly reduced the roughness to 300 nm. This method provides a flat surface (planar).

- The method of plasma roughening combined with mechanical polishing gave the smoothest surface at a rate faster than mechanical polishing alone. Below a surface roughness of about 50 nm, plasma-assisted methods appear to have no strong advantage over mechanical polishing alone.

CHAPTER 8

SUMMARY AND FUTURE RESEARCH

8.1 Summary of Findings

This study had the objective of developing microwave plasma-assisted etching techniques and understanding for diamond microstructure fabrication and diamond smoothing. This study started with characterization of both magnetized and non-magnetized discharges operating in a microwave plasma etcher. Next etching experiments to establish the etch rate, anisotropy, selectivity and surface roughness where performed to establish etching reactor operating conditions. Lastly, the polishing the MCD diamond films or plates using plasma assisted etching was studied.

8.2 Characterize the plasma-assisted etching system

The microwave plasma-assisted etcher investigated and utilized in this study was a Lambda Technologies Inc. system. The system has a 2.45 GHz microwave powered resonant cavity applicator for exciting a plasma discharge that is 25 cm in diameter. The system has a movable substrate stage that is rf biased to provide ion energy control for ion-assisted etching. Investigation of the plasma etcher included studies of its visual uniformity and its measured plasma density versus operating conditions including applicator pressure. The plasma etcher was operated in both an electron cyclotron resonance mode (ECR) using permanent magnets and a non-magnetized mode.

8.2.1 Discharge performance

The experiments demonstrated that it is possible to sustain a magnetized and nonmagnetized discharge over a pressure range from 4 mTorr- 100 mTorr. Additionally the magnetized discharge could easily be maintained even at a very low pressure of ~1 mTorr. Both magnetized and non-magnetized produced a stable, repeatable and large area high density plasma downstream (> $10^{12} cm^{-3}$) from the excitation zone. The discharge shapes was influenced by the static magnetic field formed by the permanent magnet poles such that the plasma shaped the ECR magnetic field structure. It had regions of strong light emission intensity as compared with the non-magnetized discharge. Adjusting the short and probe length combination achieved reflective power levels of ~7% of the incident power resulting in a reasonably uniform discharge. Optimized positions for both short and probe (at a pressure of 4 mTorr, a power of 700 W and gas flow rates at Ar: O_2 : $SF_6 = 6:20:2$ sccm) were 20.1 cm and 3 cm, respectively.

8.2.2 Plasma Diagnostic using SLP Probe

A single Langmuir probe (SLP) was used to measure the electron energy distribution function (EEDF), discharge plasma density and electron temperature versus pressure from 4-45 mTorr for both magnetized and non-magnetized discharges. The measurements indicated that the magnetized discharge EEDF was approximately fit to a Maxwellian profile for a low pressure of 4 mTorr. The experimental EEDF data generally falls between the Maxwellian and Druyvesteyn curves at higher pressures of 10, 15, 25 and 45 mTorr. The energy distribution with the high energy electron tail depleted may be explained from the increase of electron-neutral collisions at higher pressures. For non-magnetized EEDF measurements, the experiment data best fit the
Maxwellian distributions curve for pressures of 4-15 mTorr. At the higher pressures of 25 and 45 mTorr the EEDF falls between the Maxwellian and Druyvesteyn curves especially at higher electron energies of 15 eV or more. The high energy portion of the electron tail may be depleted as a result of inelastic collisions that deplete high energy electrons. Hence, at the lower pressures of 4 mTorr, for both non-magnetized and magnet discharges, the EEDF best fits the Maxwellian curve. For the magnetized discharge, more high energy tail depletion occurs at higher pressures of 10, 15, 25 and 45 mTorr, as compared with the non-magnet discharge.

Electron density measurements were taken at the centre of the chamber (r=0) and at a downstream position of 4 cm, over a range of pressures from 4-45 mTorr for both magnetized and non-magnetized discharges (argon flow rate of 10 sccm). For a constant absorbed power, the plasma density increased as pressure increased. The electron temperature decreased with pressure increases. The non-magnetized discharge has a higher plasma charge density as compared with the magnetized discharge

From the theory of reactive etching, a calculation based on the measured plasma discharge data showed the diamond etch rate is in good agreement with the experimental etching process. The theory etch rate is 6.63 μ m/hr and the experimental etching is from 5-8 μ m/hr at a low pressure of 4 mTorr. The theory calculation indicates that the ion enhanced chemical etching mechanism plays a critical factor in the diamond removal rate for the low pressure regime. The theoretical etching rate versus pressure plot for both magnetized and non-magnetized discharge is a good agreement with the experimental results.

8.3 Investigating the diamond etching process

Experiments to establish a diamond etching process that had good etch rate, selectivity, anisotropy and post-etch surface smoothness were performed. The inputs variables investigated include power, substrate bias, pressure, and gas mixture flow rate. The nominal etching reactor input variable settings established for diamond etching included a pressure of 4 mTorr, an input microwave power of 700 W, a substrate induced bias of -125 V and a feed gas mixture of $Ar: O_2: SF_6 = 6:20:0$ sccm. In addition to establishing a nominal set of input settings to get good etching results, systematic studies of the etch rate, anisotropic etch profile and post-etch surface roughness versus reactor input settings were performed.

8.3.1 Etch rate

The diamond etch rate increased with power, pressure and substrate bias increases. Experimental etching for three types of CVD diamond including NCD, MCD and SCD were achieved at a pressure range of 4-45 mTorr. The etch rate increased with pressure increases due to the higher charge density. The MCD diamond etch rate gave the highest etch rate as compared with NCD and SCD diamond. The SCD diamond etch rate is lowest compared with the NCD and MCD because the substrate is much thicker causing a large substrate bias voltage drop across the substrate.

A series of etching experiments were performed for both ECR and non-magnetized discharges with the rf induced dc bias varied from 0 to -200 V. The experimental results show that the diamond etching rates increased significantly with bias. For magnetized discharges, the

etch rates increased from 0.4 μ m/hr (0 V) to 10.3 μ m/hr (-200 V). And for non-magnetized discharges, the etch rates are higher from 1.6 μ m/hr (0 V) to 15.1 μ m/hr (-200 V). The explanation for this is because the non-magnetized plasma has a higher plasma density than the magnetized ECR discharge.

The etching experiments showed that the diamond etch rate increases with oxygen flow rate increases. In contrast, the diamond etches rate decreases with argon or SF_6 gas flow rate increases. The argon gas addition to the gas mixture helped stabilize the plasma. An optimized gas mixture for diamond etching is Ar: O_2 : SF_6 = 6:20:2 sccm. The diamond etch rate was repeated stably for a long period of etching time. The radial etching uniformity achieved was as low as 6% variation in etch rate across the 6 inch diameter of the substrate holder in the ECR plasma etcher.

8.3.2 Anisotropic etch

A series of etching experiments on NCD diamond were performed to investigate anisotropic etching for a pressure range from 4 to 45 mTorr. Increasing the pressure results in the diamond etch rate increasing but the anisotropic etch profile became more isotropic. High pressures caused a larger deviation from a perpendicular sidewall feature due to more collision of the ions as they cross the plasma sheath above the substrate. An anisotropic profile for NCD diamond etching of 82 degree was achieved at a pressure of 4 mTorr. 8.3.3 Mask selectivity

Five mask materials including gold, aluminium, titanium, silicon dioxide and silicon nitride were investigated for diamond selectivity. The mask layer was deposited and patterned on square 1.5 x 1.5 cm² NCD substrates with diamond thickness ~2-4 μ m. The aluminium material showed the highest selectivity (56) compared with other mask materials. The addition of *SF*₆ gas to the feed gas mixture also affected the selectivity. The etch selectivity is higher without the presence of the *SF*₆ gas, but lack of *SF*₆ made the etched surface rougher due to the spires or whiskers that formed all over the diamond etched surface. Etching with *SF*₆ gas present in the mixture leaves the etched surface smoother. The selectivity is not significantly affected by the mask feature sizes. The selectivity is also decreased when the negative substrate bias increased.

8.3.4 Etched Surface Morphology

Diamond etched without SF_6 resulted in whisker structures on the diamond etched surface. They can be produced from micro-masking effects by the deposition of hard to etch materials onto the surface. For the gold mask, the density of whiskers that appear on the etch surface is less than with other mask materials. Those whiskers can be eliminated by adding a small amount of SF_6 (2-3 sccm) into the oxygen rich gas mixture. Another phenomenon observed are randomly formed pits appearing on the etched SCD diamond surface. The distribution of these pits is not uniform and the density is in the range from 2- 7.6 x 10⁸ pits/cm². These pits have been attributed to residual defects (mainly from dislocations) in SCD diamond.

8.4 Diamond smoothing

A part of this research investigated methods to smooth MCD diamond surfaces using plasmaassisted etching combined with a sacrificial layer and mechanical lapping/polishing. Three methods studied were: 1) plasma etching combined with sacrificial layers (photoresist 1813 and Si_3N_4); 2) plasma etching combined with mechanical polishing; and 3) plasma etching with a selectivity of one combined with a sacrificial layer (SiO_2) and mechanical polishing. A highest polishing rate of up to 185 µm/hr was achieved with method 3 using a selectivity of one recipe. The lowest polishing rate used method 2 that combined plasma etching and mechanical polishing to give a rate of 120 µm/hr. All three methods showed a significant improvement of the removal rate for MCD diamond smoothing as compared with mechanical polishing only method.

It was found that by combining plasma etching and mechanical lapping/polishing, a smooth surface roughness R_a at a range of 50 nm was obtainable faster than mechanical polishing only. For surface roughness value of less than 50 nm the mechanical polishing only method worked best. The etching method with selectivity of 1, which combined plasma etching with mechanical lap/polish of the sacrificial *SiO*₂ layer, quickly reduced the roughness to 300 nm.

8.5 Future research

- 1) Diamond etch rate increases with higher values of microwave power, substrate bias, pressure and oxygen gas flow rate. Increasing those input variables more above nominal values is promising to further increase the diamond etch rate. The non-ECR plasma etching mode of operation is also promising for further increasing the etching rate. Depending on the required selectivity and anisotropic etching requirement, higher etch rates should be achievable.
- 2) Pits in the etched SCD surface are believed to be related to defects from the diamond growth. How to reduce or eliminate those pits from occurring during plasma etching is an open issue.
- 3) Methods of plasma-assisted diamond smoothing need to be further develop for smoothing thicker MCD film with a high surface roughness of 10's-100's micrometers. Higher etch rates achievable at higher pressure above 100 mTorr may be useful for diamond smoothing. The micro cracks that appear on the MCD films after the smoothing process are also a challenge for diamond smoothing.
- Etching uniformity across a large area substrate is a challenge for ECR plasma etching. Etching experiments to further investigate and improve the etch uniformity are needed.

8.6 Conclusions:

In conclusion, the Lambda Technologies etcher with 30.5 cm diameter cavity applicator has microwave mode behavior as expected from earlier work. Both ECR and non-ECR plasmas worked at low pressure in the regime regimes of 4-100 mTorr. This research presented both ECR and non-ECR plasma etching of three types of CVD diamond samples including nanocrystalline diamond, microcrystalline diamond (MCD) and single crystalline diamond. The CVD diamond samples were patterned at a micrometer scale and high etch rates and highly anisotropic profiles were obtained. A high selectivity of 56 was also obtained with aluminium as the mask material. A significant improvement of diamond removal rate for a diamond smoothing technique that used a combined plasma-assisted etching and mechanical polishing was also achieved as compared to mechanical polishing only. This research shows that plasma-assisted etching of diamond has strong potential for post processing of diamond, especially for MEMS and other electronic devices using diamond based material. BIBLIOGRAPHY

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