Chemical Study on Quarter-Micron Periodic Structure Fabrication on Si by Polarized Laser Beam on Polymer Surface and Reactive Ion Etching

BY

Cheng-Hao Lee

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Cheng-Hao Lee

APPROVED:

Prof. H. Hiraoka, Supervisor

Dr. Ian D. Williams

Prof. Nai-Teng Yu, Head

Department of Chemistry
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TABLE OF CONTENT

Title Page.................................................................i
Signature Page.......................................................ii
Acknowledgement..................................................iii
Table of Content..................................................iv
List of Figure.......................................................vii
Abstract......................................................................xi

Chapter 1:  INTRODUCTION  1
1.1 Nano-Structure Fabrication  1
1.2 Polyimide in Nano-Structure Fabrication  2
1.3 Criteria for polydimethylsiloxane in fabrication process  4

Chapter 2:  BACKGROUND  7
2.1 Plasma Etching  7
  2.1.1 Mechanisms of Plasma Etching  8
  2.1.1.1 Sputtering  11
  2.1.1.2 Chemical Etching  12
  2.1.1.3 Ion Enhanced Etching  13
2.1.2 Process Requirements  15
  2.1.2.1 Feature Size Control  15
  2.1.2.2 Selectivity  17
2.1.3 Etching Endpoint Detection
   2.1.3.1 Pressure Change
   2.1.3.2 Bias Change
   2.1.4 Effect of C_2ClF_5 in Reactive Ion Etching
   2.1.5 Oxygen Plasma Etching of Resist

2.2 The Barrel Reactor
2.3 The Planar Reactor

2.4 General Plasma Parameters
   2.4.1 Gas Pressure
   2.4.2 RF Power Input
   2.4.3 Gas Flowrate
   2.4.4 Loading Effects
   2.4.5 Temperature

Chapter 3: Silicon and Silicon Dioxide Etching in Plasma

3.1 General Chemistry and Mechanism
3.2 Typical Process Requirements
3.3 Fluorine Atom Based Plasmas
   3.3.1 The Role of Oxygen Addition
3.4 Ion vs. Free Radical in RIE process
   3.4.1 Chemisorption
   3.4.2 Ion Impact Etching
   3.4.3 Polymer formation in etching process
3.5 Carbon Containing Mixed Halogens (CF_xX_y) Plasma
Chapter 4: Polarized Laser Beam Irradiation 60
4.1 Theories For Polarized Laser Induced Periodic Structures 60
4.2 Process Requirement for Periodic Structure Formation 64
4.3 The dielectric periodic waveguide 66

Chapter 5: Experimental 68
5.1 Baseline Process on Si Wafer 68
5.2 Laser processing on polymer surface 72
5.3 Image transfer process by RIE and Plasma Etching 74

Chapter 6: Results and Discussion 77
6.1 Atomic Force Micrograph 77
6.2 Scanning Electron Micrograph 79
6.3 Etch rate experimental results 93
6.4 X-ray Photoelectron Spectra 98

Chapter 7: Conclusion 125

REFERENCE 126
LIST OF FIGURE

Figure

1.1 Contact angle measurement of water droplet on PDMSX and polyimide surface.

1.2 Temperature dependence of the viscosity of polysiloxanes.

2.1 The four fundamental mechanisms of plasma etching.

2.1a Typical pressure recording from a capacitance manometer during a plasma etch cycle.

2.1b DC bias, when etching at constant power, increases as the etch cycle progresses.

2.2 The Barrel Reactor

2.3 The Planar Reactor

2.4 Theoretical model for etch rate vs flow rate from ref (27).

3.0 Change in fluorine atom concentration and silicon etch rate with oxygen addition.

3.1 Reaction between fluorine atoms and silicon surface.

3.2 (a) anisotropic etching and (b) isotropic etching.

3.3a Polymer formation related to O₂ additions to CF₄ plasma and total pressure at constant d.c. bias voltage.

3.3b Polymer formation related to O₂ additions to CF₄ plasma and d.c. bias voltage at constant total pressure.

3.3c Polymer formation related to d.c. bias voltage and total pressure at constant O₂ additions to CF₄ plasma.

4.1 Light scattering from the polymer surface.

4.2 Interference between the incident beam and the scattered light.

4.3 The most regular periodic structure is the waveguide modes have polarization vector parallel to the polarization vector of the incident laser radiation.
4.4 The corrugated periodic waveguide.

5.1a Polycondensation reaction between a pyromellitic dianhydride and oxydianiline (Step 1).

5.1b Polycondensation reaction between a pyromellitic dianhydride and oxydianiline (Step 2).

5.2 Proposed mechanism of adhesion promotion by silane coupling agents. The silane compounds form bridges between the silicon surface and polyimide (Sequence a-d).

5.3 Fourth Harmonic Generation (266nm) occurs by generating the second harmonic of the second harmonic of the fundamental output.

5.4 Image transfer process by Reactive Ion Etching

6.1 AFM three-dimensional view of linear periodic structure on Poly(ethylene terephthalate) surface after 5 minutes exposure with 5 mJ/cm².

6.2 A SEM micrograph of a typical periodic linear structure produced by Nd: YAG 4th harmonic generation on polyimide.

6.2a A SEM micrograph of a typical periodic linear structure produced by Nd: YAG 4th harmonic generation on polyimide with 75,000 magnification.

6.3 Si{100} surface pattern of quarter-micron periodic structure after image transfer by RIE.

6.3a Surface damage pattern of quarter-micron periodic structure after SF₆-RIE.

6.3b Si{100} surface profile after overetching of periodic structure.

6.3c Structural damage of trench after RIE.

6.3d Polymer redeposition after plasma etching.
6.4 Etch rates of polyimide, PMMA resists by Reactive Ion Etching (RIE) at 13.56 MHz, 0.42 watts/cm² and dc bias of -130V. PMMA shows a significantly lower etch resistance. Aromatic polyimide has exhibit a higher etch resistance.

6.5a SiO₂ Etch Rate vs CF₄ flow rate at 100 Watts power and 0.1 torr pressure.

6.5b Silicon etch rate in RIE vs exposed silicon wafer area to the CF₄ with 8 % O₂ plasma.

6.5c Etch rates of silicon against C₂ClF₅ flowrate at pressure of 65 and 80 mtorr.

6.6 Sample wafers for ESCA analysis.

6.7 ESCA data with different gas composition of plasma treatment.

6.8 XPS spectrum of Sample 1.

6.8a XPS spectrum of Si(2p) peak.

6.8b XPS spectrum of Si(2s) peak.

6.8c XPS spectrum of C₁(2ps) peak.

6.8d XPS spectrum of C₁(1s) peak.

6.8e XPS spectrum of N(1s) peak.

6.8f XPS spectrum of O(1s) peak.

6.8g XPS spectrum of F(1s) peak.

6.9 XPS spectrum of Sample 2.

6.9a XPS spectrum of Si(2p) peak.

6.9b XPS spectrum of Si(2s) peak.

6.9c XPS spectrum of C₁(2ps) peak.

6.9d XPS spectrum of C₁(1s) peak.

6.9e XPS spectrum of N(1s) peak.

6.9f XPS spectrum of O(1s) peak.

6.9g XPS spectrum of F(1s) peak.

6.10 XPS spectrum of Sample 3.
6.10a XPS spectrum of Si(2p) peak.
6.10b XPS spectrum of Si(2s) peak.
6.10c XPS spectrum of S(2p) peak.
6.10d XPS spectrum of C(1s) peak.
6.10e XPS spectrum of N(1s) peak.
6.10f XPS spectrum of O(1s) peak.
6.10g XPS spectrum of F(1s) peak.
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ABSTRACT

A processing sequence for the fabrication of quarter micron periodic trench profiles on Si<100> wafers is described. By using polarized Nd:YAG laser irradiation on cured polyimide surfaces a periodic ripple structure is produced and a pattern transferred to a silicon substrate by reactive ion etching (RIE) without expansion of lateral dimensions. The profile has been optimized for a periodicity of 250 nm. Details of the fabrication process are described and the surface profile trench damage and plasma product deposition on the substrate are characterized by AFM, SEM, XPS respectively.
Chapter 1: INTRODUCTION

1.1 Nano-structure Fabrication

Fabrication of nano-structures on substrates such as polymers, single crystal silicon, silicon oxide, GaAs, and other electronic materials are very important both in the scientific and technical fields. These structures may be useful for alignment of liquid crystalline molecules, fabrication of quantum dots and wells, micro-mechanical devices and many others. Excimer laser-induced submicron periodic structures on polymers have been reported using a quartz polarizer to obtain polarized excimer laser beams(3, 4). These sub-micron size periodic structures were obtained under 193 nm or 248 nm excimer laser irradiation with a fluence of 2-3 mJ/cm², far below the photoablation threshold value. However, repetitive exposures to about 1000 pulses are required.

The purpose is to find a new way to fabricate nano-structures in a simple way on the polymer surfaces and also on the silicon and other semiconductor surfaces by reactive ion etching for image transfer.
1.2 The Role of Polyimides in Nano-Structure Fabrication

The potential advantage offered by polymers as dielectric insulators for microdevices has generated recent interest in the semiconductor industry. To be useful for applications, the properties of organic dielectrics must meet the engineering requirements of the device. For example, in order to avoid the structural deformation in the interconnect level, the glass transition temperature ($T_g$) of the polymer must be higher than any of the following device processing temperatures, which typically range from $200^\circ C$ to $400^\circ C$. Based on these criteria polyimide and polyimide copolymers are likely to have the necessary properties.

As semiconductor industry trends push toward the use of dry processes, polyimide plasma etching becomes the favored alternative. Plasma etching is more desirable because it provides superior results in resolution over those which can be obtained with wet etch methods. Polyimide plasma etching is comparable to photoresist etching in oxygen and oxygen mixed with small amounts of fluorine-containing gases like CF$_4$ and SF$_6$. The etch rate is a function of all the parameters associated with plasma processing, including reactor type, power, pressure, temperature, time, gas composition and loading effects. As with resist materials, polyimide etch rates vary with chemical composition.

Reactive Ion Etching (RIE) at lower pressure on high dc bias potential than conventional plasma etching is used to pattern
polyimides in anisotropic etching. These directional etch techniques can achieve the higher resolution and vertical sidewalls required for some applications. This technique can be used in multi-level resist structures.
1.3 Criteria for polydimethylsiloxane in fabrication process

The unique surface properties of the polydimethylsiloxanes (PDMS) which is important for many technical applications. These surface properties derive from the surface-active methyl groups attached to silicon which are presented to their best effect by some features of the siloxane backbone (35). The long Si-O and Si-C bonds reduce steric conflicts between methyl groups on neighbouring silicon atoms and allow unusual freedom of rotation about the Si-O and Si-C bonds. The partial ionic character of the Si-O bond allows some distortion of the large bond angle at oxygen to relieve such steric conflicts as do occur. The freedom of rotation gives a effective screening of the polar Si-O-Si backbone by the non-polar methyl groups. Thus the surface tension of PDMS is relatively lower (20.4 dyn/cm at 20°C)(52). The low intermolecular forces which characterize PDMS, result from the low surface energy of the methyl groups. The flexibility of the Si-O-Si backbone allows PDMS to adopt various configurations at different interfaces. This also explains the small temperature dependence of physical and mechanical properties of PDMS. A linear relationship for the temperature dependence of viscosity (log visc. [mPa.s] vs. Temp(°C)) may be evaluated (Fig. 1.2)(50).

The gradients of the straight lines are the measurement of intermolecular forces. If some of the methyl groups of dimethylsiloxane monomers are replaced by phenyl groups the
temperature dependence of the viscosity is increased because the intermolecular forces increase obviously. This also applies to other organic groups.

From the contact angle measurement in Fig. 1.1 shown that the water droplet on polydimethylsiloxane with the advancing angle of 117° implied the surface tension is relatively low compared with the advancing angle of 82° in polyimide.

Polydimethylsiloxane as a filler on the patterned polyimide surface forms an excellent O₂ plasma etching barrier compared with polyimide (O₂ plasma favourable).

Fig. 1.1 Contact angle measurement of water droplet on PDMS and polyimide surface.
Fig. 1.2 Temperature dependence of the viscosity of polysiloxanes. Ref.(50)
Chapter 2: BACKGROUND

2.1 Plasma Condition

A plasma is an ionized gas of free positive and negative charges. The free charge is produced by the passage of electric current through the discharge. For most plasmas for etching, the extent of ionization is very small. Typically there is only one charged particle per 100,000 to 1,000,000 neutral atoms and molecules. The positive charge is mostly in the form of singly ionized neutrals, (i.e., atoms, radicals or molecules) from which a single electron has been removed. The majority of negatively charged particles are usually free electrons; in very electronegative gases such as chlorine, fluorine, negative ions can be more abundant.

A gas that may be composed of electrons, ions of either polarity, gas atoms, and molecules in the ground or any higher state of any form of excitation, as well as of light quanta, is the definition of plasma. Plasma created by an electric glow discharge is often called low-temperature plasma to distinguish it from hot plasma. Generally, plasma is generated by combustion, flames, electric discharge, controlled nuclear reactions and other means. Because plasma loses energy to its environment mainly in the form of radiation and through conduction to the reactor wall, plasma energy must be supplied as fast as it is lost by continuous electric discharge.
2.1.1 Mechanisms of Plasma Etching

Many factors play a role even in the simplest examples of plasma etching. However, plasma etching mechanisms can be classified into four functional categories.

The first mechanism is sputtering. As shown in Fig. 2.1a, positive ions are accelerated across the sheath and strike the substrate with high kinetic energy. Some of this energy is transferred to surface atoms which will be ejected, thus leading to material removal. This process is distinguished from the other mechanisms in that the interaction is mechanical.

Second, simple chemical etching occurs when active species from the gas phase encounter a surface and react to form a volatile product(Fig. 2.1b). Since high product volatility is essential, without volatility the reaction products would deposit on the surface and prevent gaseous species from reaching it, and later cut off the etching reaction. In chemical etching, the role of the plasma is merely to supply etching species -- usually in the form of free radicals. This type of etching shares the characteristics of common chemical reactions. Etching is usually non-directional, since ion bombardment would not be involved, and selectivity can be extremely high due to large differences in an etchant's chemical affinity for various substrate materials.

Third, the ion-enhanced energetic etching (Fig. 2.1c), neutral species cause little or no etching without ion bombardment. Ions "damage" the substrate material, making it more reactive toward incident neutral radicals. The term
“damage” includes diverse processes such as the formation of highly reactive dangling bonds, the lattice structure damage and formation of dislocations, injection of adsorbed reactant into a lattice by collision, or bond-breaking in intermediate adsorbed surface compounds. In fact, there is no universal mechanism for ion-enhanced energetic etching, but it is true that the ions supply kinetic energy, which disrupt the etched surface structure. The ions strike surfaces vertically, the etching induced is directional.

Fourth, inhibitor-driven ion-enhanced etching. (Fig. 2.1d) In this etching by neutrals is spontaneous and ion bombardment is not involved in the etching mechanism. Ions play out their role by interacting with a second ingredient—film formers, which can deposit on substrate and sidewall surfaces and retard the rate of the etching reactions.
Fig. 2.1 The four fundamental mechanisms of plasma etching are:

a) sputtering
b) chemical etching
c) ion-enhanced energetic etching
d) ion-enhanced inhibitor anisotropic etching
2.1.1.1 Sputtering

Sputtering is a universal way to etch material by plasma action. The ejection of material occurs when positive ions are propelled into substrate surfaces by the negative potentials at the edge of a plasma. When an ion transfers energy to a small region of the substrate at the point of impact, some substrate molecules receive enough energy to be ejected from the surface. Under low pressure conditions, material is removed as it is thrown across the reactor volume (low pressure and long mean-free path are required for material to leave the surface without being backscattered and redeposited).

Sputtering is non-selective because the ion energy required to eject material is large compared to differences in surface bond energies and chemical reactivity. For many applications the non-selectivity means that sputtering cannot be used.

Sputtering suffers from other disadvantages. It is generally slow compared to other types of etching. The etch rates are limited to several tens of nanometers per minute compared to the hundreds of nanometers per minute achieved by chemical and ion-assisted etching.
2.1.1.2 Chemical Etching

In chemical etching, the only function of the plasma is to maintain a supply of gaseous etchant species. However, it is the most selective mechanism, since unwanted reactions will not take place at all when their thermodynamics are unfavorable. By contrast to sputtering, where involatile materials can be ejected away, a volatile reaction product is necessary for chemical etching. Involatile products would accumulate on the surface and passivate it against further reaction.

Purely chemical impact, unlike other forms of plasma etching, is always non-directional. Thus, when a silicon substrate reacts with atomic fluorine, etched areas are undercut with a characteristic isotropic circular profile.

Chemical etching is advantageous in applications where under-cut limited linewidth is not a critical problem. Examples include oxygen plasmas are used to strip resist masks isotropically after the pattern transfer step.
2.1.1.3 Ion Enhanced Etching

Plasmas differ from ordinary liquid and gaseous reacting media in that a directional negative-going potential always forms along the plasma boundaries. This sheath field, an electric field, propels positive ions into boundary surfaces at normal incidence. Hence, there is an anisotropic ion flux at plasma-solid boundaries. Under the appropriate conditions, this ion bombardment stimulates directional etching. However, this etching was thought to be caused by chemical reactions between the ions and surface material. It is acceptable that anisotropic plasma etching is brought by the action of neutral gas-solid reactions, which are stimulated or directed by ion bombardment. However, there are two types of ion-enhanced etching: (i) Energy-driven anisotropic ion-enhanced etching. (ii) Inhibitor-driven anisotropic ion-enhanced etching. In energy-driven ion-enhanced etching, reactions between the substrate and neutral species from the gas phase are accelerated by ion bombardment. In inhibitor-driven anisotropic ion-enhanced etching a surface-covering agent protects the vertical sidewalls of features from reactive neutrals, while ion bombardment suppresses inhibitor growth on the horizontal surfaces that are etched. This mechanism requires three features: (I) a reactive neutral etchant gas species, (II) an ion-flux to the surface, and (III) an inhibitor film species. Inhibitor-driven etching differs from energy-driven ion-enhanced etching in that the etching reaction is spontaneous, even without ion bombardment. The vertical ion flux either prevents the films from forming, or cleans them as
they grow. Generally, low ion energies keep the horizontal surfaces free of inhibitor and allow further etching. By contrast, high energetic ions are usually required to enhance etching with damage on the surface profile. Inhibitor species may be formed by a variety of sources. Some fluorinated feed gases yield unsaturated polymer forming species in plasmas. By unsaturated species it means CF$_2$ radicals and derivatives formed by chain building oligomerization. These simple monomers and oligomers polymerize to form thin films on surfaces and trench sidewalls which induce anisotropic etching. (35)
2.1.2 Process Requirements

2.1.2.1 Feature size control

Semiconductor device fabrication of nanoscale size features demands strict control of the etch bias and high aspect ratio pattern generation by reactive ion etching. When the aspect ratio is extremely high, neutral radicals, energetic ions and etch products must experience the difficulty of either reaching the bottom of a trench or escaping from the trench. Consequently, the etch rate of the trench would decrease continuously as RIE progresses, and eventually the etching reaction would stop if the trench is too deep. When silicon trenches of different sizes are etched by a single RIE run, their etched depth should vary with the trench width because a wider trench tends to etch faster than a smaller one. In a RIE experiment with Si trenches (14), the etched depth was found to be proportional to the width when the RIE time was constant. This feature size dependence of etch rates is called RIE lag, meaning that etching of a narrow trench lags behind a wide trench. Conceivably the RIE lag may result from many different physical factors. ion-neutral collisions at the sheath (18,19) could deflect ions, only a small fraction of the ions can reach the bottom of the narrower trench. When a low dielectric polymeric material that contains Si-O bonds is used as an etch mask, the electric field can be locally perturbed by a charge build up at the top polymeric surface, therefore reflecting ions toward the mask (29) in a way inversely
proportional to the trench width. Another possible mechanism is that the transport of the reactive neutral species can be limited by the trench geometry in analogy to conductance in a vacuum system (31). All those mechanisms can lead to RIE lag, suggesting that RIE lag could minimised or even disappear in a low pressure RIE process.

Reactive ion etching involves two competing reactions (33): directional etching along the path of the incident ions and isotropic etching of a purely chemical nature. A balance between these two etching mechanisms ultimately determines the slope of the etched sidewall. In order to achieve a high aspect ratio, it is necessary to rely on the ion-driven directional etching, thus minimizing the isotropic etching mostly associated with the neutral radical species. In Si trench RIE, one must avoid contamination with F atoms because of their high isotropic etching reaction. Another way to minimize the isotropic etching is to passivate the sidewall by depositing a plasma by-product. Even in the sidewall passivation, ion bombardment is necessary to suppress the deposition of the passivating layer at the bottom surface of the Si trench, so that the radical species may react with Si to support the etching process. Therefore, it is a good assumption that the ion transport inside a trench should play an important role in the RIE lag.
2.1.2.2 Selectivity

Selectivity, that is the etch ratio between materials, is a
critical figure of merit. Theoretically, there are two kinds of
selectivity, (i) selectivity for etching a substrate rather than
the pattern mask (resist durability), and (ii) etching selectivity
between two material layers. Roughly, the minimum required
selectivity is simply the thickness ratio between two material
films. It is determined by the amount of material removal that
can be tolerated, however, not the total film thickness. This
value can range from a small fraction up to 50 % of a layer.

The selectivity requirements for plasma etching based on
work by Mogab (37). It is assumed that etching can have both
isotropic and anisotropic components and there is undesired
plasma erosion of both the mask and the substrate underneath
the layer that is patterned.
2.1.3 Etching Endpoint Detection

Normal surface topography includes changes in film thickness that require some degree of overetching. Yet overetching must be done with great care. Planar areas, which often have the thinnest film, are sensitive to excessive overetching because that is where sensitive layers such as extremely thin oxides (=150 Å) are found. These areas require high selectivity between the film being removed and the substrate material. Since some anisotropy must be compromised for high selectivity, it is important to limit the degree of overetching with the required selectivity. Thus, endpoint detection is an important part of process control.

The sequence of events in a typical plasma etch process provides several ways to detect the endpoint. When RF power is first introduced, the etchant species are produced. After some latency, these species react with the film to produce a volatile product. Toward the end of the etch cycle the underlying substrate begins to be exposed and reactions with the etchant produce new secondary products, which can be detected.
2.1.3.1 Pressure Change

Because the gas is heated and dissociated when RF power is applied, the pressure tends to rise initially. When etching is fully underway, the gas-solid etching reactions usually cause a decrease in the number of gas molecules so system pressure will fall if there is a constant resistance to flow (fixed orifice). Generally, this pressure decrease is about 5-10%. Figure 2.1a shows these effects schematically. One problem with pressure monitoring is that changes in the etching process are sometimes caused by pressure changes.

Fig. 2.1a Typical pressure recording from a capacitance manometer during a plasma etch cycle (with constant pumping speed). When power is turn on, the pressure rises until the film starts to etch. Pressure falls to a lower value during etch process and increases as the film clears at the endpoint.
2.1.3.2 Bias Change

As the gas composition changes during the etch cycle, the plasma impedance and sheath characteristics change. This causes changes in the self-bias voltage which is generated in different reactor geometries. Fig. 2.1b shows the bias change during a resist or polymer strip cycle. The bias reaches a maximum as the film starts to clear and then decreases.

Fig. 2.1b DC bias, when etching at constant power, increases as the etch cycle progresses. The rate of increase bias of voltage drops as film clears, then bias continue drops during the overetch period.
2.1.4 Effect of $\text{C}_2\text{ClF}_5$ in Reactive Ion Etching

When substrates are subjected to plasma, an accelerated particle bombardment takes place which produces a physical damage to the surface similar to the radiation damage produced by a low-energy ion implantation. It has been proved that impurities are incorporated to the crystal, and RIE develops extrinsic dislocations in the silicon lattice.

When there is no $\text{C}_2\text{ClF}_5$ in the plasma, fluorine atoms easily penetrate in the silicon lattice, yielding high density of deep levels. On the other hand, Mieth et al. (5) have demonstrated that when the plasma contains $\text{C}_2\text{ClF}_5$, carbon atoms induce the deposition of a polymeric film, and then the fluorine radical penetration becomes lower. For these reasons, deep level densities are higher for SF$_6$ plasma than for SF$_6$ plasmas containing $\text{C}_2\text{ClF}_5$. 
2.1.5 Oxygen Plasma Etching of Resist

Oxygen plasmas are used to etch resists both isotropically and anisotropically. Isotropic resist stripping with O atoms is one of the traditional plasma applications, while anisotropic pattern transfer was developed to permit micron- and submicron pattern transfer using the "trilevel" process (39). Oxygen chemical treatment is also used to passivate metal and silicon-bearing resists for bilevel lithography and to remove epoxy smears from holes in multilayer printed circuit boards.

At moderate pressure and high frequency, a discharge in pure oxygen produces oxygen atoms. These atoms attack organic materials to form CO, CO₂ and H₂O as the final end products (12). The main degradation mechanism appears to be random chain scission (40). Stripping rates in pure oxygen plasmas are proportional to oxygen atom concentration (41,42). Inert gas additions can help stabilize O₂ plasmas. Chemical attack of resists in oxygen plasmas is much influenced by the structure and substitutional groups on the polymer, and also by several physical variables such as temperature. The temperature dependence of attack in an oxygen plasma may also depend on the resist's glass transition temperature (T_g). For example, the apparent activation energy of poly(methyl methacrylate) (PMMA) etching in O₂ plasma increased sharply from 4.4 kcal/mole below the glass transition temperature, T_g (60-90°C), to ≈9.7 kcal/mole above T_g (43). Activation energies between ≈5-15 kcal/mole have been measured for resist oxidation under
chemical attack by O atoms, depending on the particulars of the resist and other physical conditions.

Stripping rates are enhanced when fluorinated gases are added to an oxygen plasma. Even a few percent of CF$_4$ or SF$_6$ added to O$_2$ can bring about a large increase in the removal rate for many resists. The enhancement seems to be caused by two effects (41,44): (i) fluorine atom reactions produce reactive sites on the polymer backbone, and (ii) small amounts of fluorine increase the concentration of atomic oxygen in an oxygen plasma (45,46). Atomic fluorine abstracts hydrogen from organic polymers, leaving unsaturated or radical sites. These sites are much more susceptible to oxygen than a saturated polymer chain. When oxygen attacks these sites there is chain scission, carbonyl groups are formed, and the polymer is converted into volatile oxidation products. The initial steps in fluorine-assisted degradation are probably similar to

\[ \text{F}^* + \text{C}-\text{C}-\text{C}-\text{C} \rightarrow \text{HF} + \text{C}^*\text{C} \]
followed by

\[ \cdot O + \begin{array}{c} \cdot \\ C - C - C - C \\ H - H - H \end{array} \rightarrow \begin{array}{c} \cdot \\ C - C - C - C \\ H - H - H \end{array} \]

\[ \rightarrow \begin{array}{c} O \\ C - C \\ H \end{array} + \begin{array}{c} \cdot \\ C - C \\ H \end{array} \]

The energy liberated when fluorine abstracts hydrogen can cleave carbon-carbon bonds (48) and is probably a primary degradation mechanism in plasmas containing a high concentration of fluorine (e.g. CF\(_4\)/O\(_2\) or SF\(_6\)/O\(_2\)) (49).

With polymers that contain unsaturated backbone groups, fluorine addition reactions may contribute to the degradation:

\[ F^\cdot + \begin{array}{c} H \\ C - C = C - C \\ H \\ H \end{array} \rightarrow \begin{array}{c} \cdot \\ C - C - C \\ H - H \end{array} \]
The radical sites are then oxidized as before. Curiously, there is a shift from an oxygen-dominant etch mechanism to fluorine-dominant degradation in the etching of polyimide by SF$_6$/O$_2$.

Two mechanisms have been proposed to explain the increase in atomic oxygen and these may play an important role. Actually, recombination of O atoms to O$_2$ on reactor walls is the dominant loss process for O atoms. It is expected that F$_2$ lowers the rate of O atom recombination on walls. A second proposal is that the added halocarbon changes the electron energy distribution function (10) in a way that favours oxygen atom production.
2.2 The Barrel Reactor

The barrel reactor was the first type of plasma etcher to be used for semiconductor production purposes and it was derived from an earlier reactor used for plasma oxidation of organic materials, e.g. "plasma ashing" (6). In this reactor an oxygen plasma at pressures between 2 - 10 torr was sustained by an rf potential applied to two external electrodes. These systems were used to remove photoresist and other carbonaceous materials by oxygen reaction in a plasma. The apparatus was modified for silicon wafer etching by placing an aluminium mesh tunnel around the wafers, which were stacked on long carriers as shown in Fig. 2.2. The wafers are mounted vertically in the reactor chamber and thermal contact is not available for controlling their temperature. Some temperature control is achieved by preheating the wafers in an inert gas plasma before the etching is commenced. Overheating of the wafers gives rise to poor uniformity of etching, poor selectivity in the etching of different layer materials, non-reproducible etching rates and resist deterioration. The electron and ion bombardment of a body exposed in the plasma media can cause undue temperature rise without external cooling. The introduction of an aluminium tunnel surrounding the wafers appears to reduce the wafer heating and improves process conditions.

In a barrel reactor where ion bombardment has a small role in the etching process, for example, the etching selectivity for Si:SiO₂, is as high as 100:1. However barrel reactors suffer a
serious disadvantage because, as etching mainly depends on free radical reaction, they etch isotropically and cannot be used where linewidth loss is critical.

Fig. 2.2 The Barrel Reactor
2.3 The Planar Reactor

The planar plasma reactor is widely used for etching semiconductor materials. It was developed from the work of Reinberg (7) and Heineke (8). The system using parallel plate electrodes was an important development because it provided the capability under some conditions for anisotropic etching. A typical reactor consists of a top electrode connected via an insulated feed through to an rf supply and a bottom electrode which is normally grounded, (Fig. 2.3). The wafers rest on the ground electrode and are immersed in the plasma. The top electrode is normally capacitively coupled via a blocking capacitor to the rf supply. In this system each electrode is negatively biased with respect to the plasma and generally the negative bias is higher on the top electrode, as shown in the experimental studies.

It is noted that a planar reactor will etch wafers located on either electrode surface and in some cases will etch wafers faster on the top rf electrode due to the larger negative bias developed on the top electrode. The work surface is the grounded electrode which forms an adjacent ion sheath because of the negative bias developed with respect to the plasma potential. Thus the wafers placed on the ground-electrode are bombarded by atomic and molecular ions which have been accelerated in the ion sheath as well as low energy electrons. The wafers are also exposed to free radicals and molecular fragments produced in the plasma volume.

Planar reactors have some disadvantages compared with
barrel reactors, e.g. higher cost, poor selectivity, smaller wafer throughput. The poor selectivity is because of physical sputtering from the ion bombardment contribution which also produces heating effects that can result in poor etching uniformity, rapid removal of photoresist, and resist 'flow' if heating is too excessive.

Production planar etchers have cooled electrodes in order to attempt to improve the uniformity and increase the polymer lifetime during etching.

![Diagram of the Planar Reactor](image)

**Fig. 2.3** The Planar Reactor
2.4 General Plasma Parameters

2.4.1 Gas Pressure

The manner in which reactive ion etching depends on plasma pressure is complex as many effects occur simultaneously. As the gas pressure is raised there is a reduction in the mean free path of the plasma components producing more radicals and ions. The increase in free radical and ion production will have several effects. For instance, it can increase the etch rate of the wafer by raising the ion or free radical concentration at the surface of the wafer. On the other hand free radicals can recombine with each other forming higher molecular weight species, e.g. from fragmented CF₄ molecule one can obtain:

\[ \cdot\text{CF}_3 + \cdot\text{CF}_3 \rightarrow \text{C}_2\text{F}_6 \]  

The dimers can also fragment and recombine eventually forming high molecular weight condensed polymers on the surface. Such an event is more probable at higher pressures, and with long resident times for free radicals of heavy mass.

When increasing the pressure the ion concentration may initially increase and thus the impedance of the plasma may drop resulting in a lower applied potential at a given power input. At the ion sheath the ion bombardment energy will fall with the decrease in sheath potential caused by the reduction of applied
potential to the plasma. Polymers may grow on the exposed surface if the ions arriving have an energy below the sputtering threshold to remove the polymer from the surface. Also the ion energy may be too low to induce chemical reactions for ion bombardment.

The increase in ion density at a given power input with a rise in pressure is due to the increase in collision rates between the electrons and gas molecules and between ions and neutrals. The pressure rise will also increase the ionization and recombination reactions in the plasma, it may also increase the collisions between ions and neutrals, thus reducing the ion energy impact with the electrode surface. Increasing the operating pressures of plasmas may also increase the rate and type of species that could physically or chemically adsorb on the wafer surface. Finally, it will change the rate-controlling step in semiconductor etching processes.
2.4.2 RF Power Input

At constant pressure the plasma density can be raised by increasing the power input into the plasma. This increase in power will cause a rise in the applied potential especially at lower pressures (15). It will also increase the potential across the ion sheath, resulting in raising the ion bombardment energy. Any increase in power input will also increase the rate of formation of other plasma products such as free radicals. However, any polymer condensation from heavy free radicals will be offset by the higher ion bombardment energy.

In a plasma excited by a low frequency power supply the discharge is sustained mainly by ion induced secondary electron emission at the electrodes. An increase in ion bombardment energy will not significantly change the secondary emission coefficient. However, the larger potential developed across the ion sheath with increasing applied potential will accelerate secondary electrons from the electrode surface out into the plasma with larger energies. The increase in electron energy may both raise the ion density and change the ratios of ions to free radicals, on the other hand, both the ion and free radical concentration will increase. The degree of etch rate rises with increasing rf power input depending on whether the interaction is controlled by ion bombardment or free radical species.

The increase in ion bombardment energy by increasing rf power input could make the ion bombardment at the surface inducing chemical change by bond cleavage. There will also be an increase in ion density, which will increase the rate of material
being removed from the surface. Alternatively, if the reaction is rate limited by a free radical process, increasing in ion energy or density alone may be insignificant. Thus, etching will be enhanced by a rise in free radical concentration in the plasma.

The rf power input to the plasma must be carefully controlled because it governs the ion current and is also the major source of thermal energy. In rf plasmas the current flowing in the dark space sheath is expressed in two components conduction, (i) charge flow; (ii) from cycle changes of the discharges across the sheath.
2.4.3 Gas Flow-rate

The dependence of gas flow-rate on the etching rate of specific wafer surface varies from plasma reactor to plasma reactor. However, below a critical flow-rate, there is an inadequate supply of reactant gas to etch the wafer and thus a small increase in flow-rate can rapidly increase the etch rate of wafer.

As the flow-rate is raised the product species are flushed away and subjected to less dissociation and recombination reactions in the plasma but at the same time the initial reactant gas is less utilized (27). Use of the etchant gas will increase as the rf power input is increased (27). If the gas flow-rate is further increased with an accompanying increase in pumping speed in order to give a constant system pressure then it is possible that the active species produced in the plasma can be pumped away before they have the opportunity to react. The foregoing effects are illustrated in Fig. 2.4 in relation to the etch rate observed.

The time in which a plasma species spends in the system reactor before being pumped is known as the 'residence time' (t). This is relevant to the volume of the chamber (V) and the pumping rate S, and is directly related to the flow rate.

\[ t = \frac{V(\text{litres})}{S(\text{litres per sec})} \]

The pumping rate is related to the system geometry and pressure, and in many processes the resident time will not be
reached by an active species because it is reacting and being consumed thereby producing other products. Residence times for molecules in process systems can vary between 0.5 to 50 seconds for which they are not consumed (28).

Fig. 2.4 Theoretical model for etch rate vs flow rate from ref (27).
2.4.4 Loading Effects

Loading effects result from producing a limited supply of etching species in the plasma. A typical example is the etching of silicon in a barrel reactor in a CF$_4$/O$_2$ plasma when the etch rate is reduced by the addition of more silicon wafers. The effect arises from the large area of silicon present for reaction with the active fluorinated species.

The loading effects can vary depending on the pressure, species present and their resident time in the plasma. Any changes occurring in the gas phase may cause changes in any surface compound formation in which ions may be activated or sputtered. If the active free radicals in the plasma have a high recombination rate, they will react together before they have a chance to etch the wafer and the active free radical concentration will be low. A low concentration of active free radical species in the plasma compared with the ion etching component will result in a smaller loading effect in the reactor system. It will also reduce the lateral etch component in a plasma etching process resulting in an increase of anisotropy.
2.4.5 Temperature

The rate of etching depends on temperature because the chemical reaction involved is subject to an activation energy and also because the surface coverage of chemisorbed species is temperature dependent. Substrate cooling is necessary to protect the polymer or photoresist during etching against thermal deterioration and viscous flow. However, substrate cooling can also give consistent etch rates in etching processes since the wafer temperature can be kept constant.

The dependence of etch rate on temperature will be less in processes where the etching proceeds mainly by ion bombardment in the presence of active species such as in a planar reactor, where the ion impact provides the activation energy.

Holland (1) discusses the etching of carbon in a planar reactor using an oxygen plasma. Holland mentioned that ion bombardment removes the carbon surface by chemical sputtering which provides the activation energy to form a volatile carbon monoxide (CO) product and the reaction rate can be enhanced by oxygen implantation in the carbon surface. Therefore, in reactive ion etching the effect of temperature will depend on how much wafer etching arises from free radical reactions and how much arises from ion impact reactions.

Schwartz (20) has observed a decrease in etch rate with increasing wafer temperature. She suggested that a rise in temperature reduces the number of adsorbed species on the wafer surface otherwise it would be available for etching when
activated by ion bombardment.

Using Arrhenius plots of the silicon and silicon dioxide etching rate in atomic fluorine, Flamm (25) has measured activation energies for Si and SiO₂ which he found to be 0.108 eV/mol and 0.163 eV/mol respectively. The atomic fluorine was produced in a molecular fluorine plasma from which Flamm also estimated the ratio of Si to SiO₂ etching by fluorine atoms to be

\[(4.74 \pm 0.49) \exp(-0.055 \text{ eV}/\text{RT})\]

At a temperature of 25°C (298°K) and \( R = 0.00862 \text{ eV/mol/°K} \), the ratio of Si to SiO₂ etching is thus approximately 5.12 to 1.

The values of activation energy may vary from one investigation to another. This is probably due to the difficulty in measurement of small activation energies in a narrow temperature range. For silicon this effect may also depend on the orientation (100; 111; 110), and different sample surface areas being used giving rise to loading effects.

Much of the RF power dissipated in the plasma ultimately appears as thermal energy and is the major source of temperature rise (26). In planar reactors, the electrodes should be temperature controlled by cooling water and good thermal contact with wafers in order to provide an improvement in uniformity, particularly where there is a large free radical etching component.
3.1 General Chemistry and Mechanism

$\text{CF}_4$ gas will not react with silicon or silicon oxide since the energy requirements are insufficient for a reaction to proceed kinetically. Using thermochemical data, simple calculations can be made to assess if a reaction is energetically favourable to proceed.

For example, the dissociation energy of a C-F bond in $\text{CF}_4$ is 439 kJ/mole and for a Si-Si bond in silicon is 176.4 kJ/mole. If a reaction were to proceed then fluorine would react with the silicon to form the stable volatile product silicon tetrafluoride ($\text{SiF}_4$), which has a high bond dissociation energy of (Si-F) 543.4 kJ/mole and carbon deposit with C-C bond energy of 346.9 kJ/mole.

The energy balance for the reaction would be:

$$2 \text{C---F} + \text{Si---Si} \rightarrow 2 \text{Si---F} + \text{C---C}$$

<table>
<thead>
<tr>
<th>Bonds Broken Energy in</th>
<th>Bonds Formed Energy Out in kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(439 kJ)</td>
<td>176.4 kJ</td>
</tr>
<tr>
<td>2(543.4 kJ)</td>
<td>346.9 kJ</td>
</tr>
</tbody>
</table>

$\Delta H = -32.4 \text{ kJ/mole}$
The reaction is thermodynamically allowed ($\Delta H = -32.4$ kJ/mole), however the energy barrier associated with breaking the C-F bond is very high, leading to very unfavourable reaction kinetics. Hence CF$_4$ gas will not react directly with silicon at an appreciable rate. However, in a CF$_4$ plasma the high energy electrons collide with molecular bonds and rupture the C-F bond generating reactive ion species such as excited fluorine and CF$_3^-$ radicals as well as ions; e.g.

$$\text{CF}_4 + \text{e}^- \rightarrow \text{CF}_3^- + \text{F}^- + \text{e}^-$$

$$\text{CF}_3^- \rightarrow \text{CF}_3^- + \text{e}^-$$

$$\text{CF}_4 + \text{e}^- \rightarrow \text{CF}_3^- + \text{F}^- + 2\text{e}^-$$

CF$_4$ plasmas are a cheap, simple source for generating active species such as F$^-$ and molecular fluorine which will react with silicon to form SiF$_4$. The energy balance is shown by:

$$2\text{F}^- + \text{Si-Si} \rightarrow 2\text{Si-F}$$

176.4 kJ \hspace{1cm} -2 \times 543.4 \text{ kJ} \hspace{1cm} \Delta H = -910.4 \text{ kJ/mole}$$

(Molecular Fluorine)

$$\text{F--F} + \text{Si--Si} \rightarrow 2\text{Si--F}$$

153 kJ \hspace{1cm} 176.4 kJ \hspace{1cm} -2 \times 543.4 \text{ kJ} \hspace{1cm} \Delta H = -757.4 \text{ kJ/mole}$$
and for SiO₂, with a bond strength of Si--O, 369.5 kJ per mole

\[ \text{F--F} + \text{Si--O} \rightarrow \text{Si--F} \]

153\text{kJ} \quad 369.5 \text{kJ} \quad -543.4 \text{kJ}

\[ \Delta H = -20.9 \text{kJ/mole} \]

\(\Delta H\) is the standard enthalpy of formation which is the amount of heat flowing into or out of the reaction system when a compound is formed from the elements under standard conditions (1 mole, 1 atm pressure at 25°C). A negative \(\Delta H\) value indicates that energy is liberated from the system i.e. the reaction is exothermic, with 1 mole of silicon is 757.4 kJ per mole but for 1 mole of \(F₂\) reacting with 1 mole of SiO₂ \(\Delta H\) is only 20.9 kJ per mole. Thus it is not surprising that the reaction between \(F₂\) and Si is far more preferrable to the reaction between \(F₂\) and SiO₂. There is a small increase in \(-\Delta H\) when considering SiO₂ reactions with F* radicals. Also with the presence of CF₃* radicals the energy favourability may improve still more with the possible formation C=O bonds (723.14 kJ per mole):

\[
\begin{align*}
\text{F} & \quad \text{C}^* & \quad \text{Si} & \quad \text{Si} & \quad \text{F}^* \\
439 \text{kJ} & \quad 2 \times 369.5 \text{kJ} & \quad 723.14 \text{kJ} & \quad 2 \times 543.4 \text{kJ}
\end{align*}
\]

\[ \Delta H = -632.02 \text{kJ/mole} \]

In principles of thermodynamics, \(\Delta H\) is used to estimate \(\Delta G\) values, e.g.

\[ \Delta G = \Delta H - T\Delta S. \]
where ΔG is Gibbs free energy change (kJ) which is the indication of the driving force of the reaction and is the degree of irreversibility if ΔG has a negative value. T and ΔS are the temperature (°K) and entropy change (kJ/mole/°K) respectively. However, this can be an simplified view of the energy changes during a reaction. Reactions should thus be considered not only thermodynamically but jointly with respect to the kinetics of the mechanism.
3.2 Typical Process Requirements

For device fabrication the silicon to be etched can be a wafer (single crystal) or a layer of polysilicon used for MOS gate arrays. The etching normally requires selectivity to favour a fast etch rate for silicon with the minimum loss of the SiO$_2$ substrate. This can be achieved by using a CF$_4$ + 8% O$_2$ plasma in a barrel reactor, with good selectivity between silicon and SiO$_2$, but the etching is isotropic. In a planar reactor, a CF$_4$ plasma etches less isotropically but also reduces the selectivity between silicon and SiO$_2$. Good selectivity between Si and SiO$_2$ and an anisotropic silicon etch can be achieved by using a chlorine plasma; but there is usually poor selectivity between silicon and the masking resist (polymer) layers.

In some device processes the SiO$_2$ layer is required to be etched in favour of an underlying silicon layer which may have sensitive device regions. Using a CF$_4$ plasma in a planar or barrel reactor does not usually provide sufficient selectivity. However, by increasing the carbon to fluorine ratio in a plasma, i.e. by using C$_2$F$_6$ gas in a planar reactor, the selectivity begins to improve and by C$_3$F$_8$ the SiO$_2$ layer can be etched in a planar reaction about eight times faster than the silicon layer.
3.3 Fluorine Atom Based Plasmas

3.3.1 The Role of Oxygen Addition

Mogab (36) first observed that when small amounts of oxygen were added to a CF$_4$ plasma the etch rate of silicon increased dramatically and the etch rate of SiO$_2$ only increased slightly, resulting in a selectivity of 10:1.

Mogab (36) used a planar reactor with a 13.56 MHz RF supply and a mass spectrometer analysing the gas in the effluent line. An optical emission spectrometer was used to observe the electronically excited F atoms with a sapphire window for viewing the plasma. Mogab observed an increase in the optical emission intensity with the increase in the fluorine atom concentration [F$^*$] and correlated this quantitatively with the increase in the silicon etch rate on addition of oxygen to the CF$_4$ plasma. Mogab concluded that the F$^*$ atoms were the main etching species. The increase in the silicon etch rate peaked at 12% oxygen addition and the fluorine concentration [F$^*$] increased to a peak at 23% oxygen addition as shown in Fig. 3.0.
Oxygen atoms do not react with CF₄ gas alone as the enthalpy of the compound formation is insufficient. However, oxygen can react with dissociated CF₄ plasma products and can inhibit fluorine recombination reactions, typically by controlling the surface to limit three-body collision recombinations:

\[ \text{e.g. } F^* + F^* + M \text{ wall } \rightarrow F_2 \]
\[ \text{CF}_3^* + F^* + M \text{ wall } \rightarrow \text{CF}_4 \]

An example of wall poisoning is the case when small amounts, 0.1%, of gaseous H₂O were added to oxygen plasma from which an increase in free radical concentration [O⁺] was observed (38). This is due to surface poisoning by gas additions preventing three-body recombination events. The mass spectrometer used by Mogab showed that silicon oxyfluoride was not formed in CF₄/O₂ plasma but more stable products of CO, CO₂ and COF₂ were observed. The role of oxygen is to scavenge the CF₃⁺ radicals thus preventing recombination with F⁺ radicals. Mogab stated that the silicon etch rate was not exactly proportional to \([F^*]\) because of the competition between excited F atoms and O atoms for the active sites on the silicon surface. Chemisorption of oxygen atoms on the silicon surface will reduce the etch rate and at the same time the presence of oxygen raises the \([F^*]\) by preventing the following recombination reactions:

\[ \text{CF}_3^* + F^* \rightarrow \text{CF}_4 \]
\[ \text{CF}_3^* + \text{CF}_3^* \rightarrow \text{C}_2\text{F}_6 \]

(small unless \([\text{CF}_3^*]\) is high)
\[ \cdot \text{CF}_2 + F_2 \rightarrow \text{CF}_4 \]

Prevention of recombination of the fluorocarbon species by the scavenging action of \( \text{O}_2 \) and \( \text{O} \) is effective. Also the \( \text{C}=\text{O} \) bond has a high energy of formation and stable products such as \( \text{COF}_2 \) can be formed as follows:

\[ \cdot \text{CF}_3 + \text{O}_2 \rightarrow \text{COF}^* + \cdot \text{OF} \]

\[ \cdot \text{CF}_3 + \text{O}^* \rightarrow \text{COF}_2 + \text{F}^* \]

\( \cdot \text{OF} \) is unstable and decomposes either by the process

\[ 2\cdot \text{OF}^* \rightarrow 2\text{F}^* + \text{O}_2 \quad \text{or} \]

\[ \cdot \text{OF} + \cdot \text{CF}_3 \rightarrow \text{COF}_2 + 2\text{F}^* \]

The addition of oxygen to \( \text{CF}_4 \) plasma may also affect the ionization condition of the plasma.

Note: \( \text{F}^* \) is a neutral fluorine radical

\( \cdot \text{CF}_2 \) is a triplet species formed in \( \text{CF}_4 \) plasmas with two unpaired electrons.
Fig. 3.0 Change in fluorine atom concentration and silicon etch rate with oxygen addition. (36)
3.4 Ion vs. Free Radical in RIE process

Coburn and Kay (21) and other workers (22,23) proposed that, in the etching of silicon in a CF$_4$ plasma, there was a co-operative interaction between ion bombardment and free radicals. Ion bombardment may remove any carbonaceous deposits and damage the surface, thus increasing the probability for a free radical to react with the exposed and weakened silicon bonds. Winters (16) observed that neutral CF$_3$ radicals (generated from a CF$_4$ plasma) have a relative reaction probability of only 0.25 whereas CF$_3^+$ has an absolute reaction probability of 1 on a clean silicon surface. His results show that the ions react with silicon and thus influence the etch rate considerably.
3.4.1 Chemisorption

In section 3.1 the bond energies of Si--F (543.4 kJ per mole) reveal a thermodynamically favourable reaction for:

$$4F^* + \text{Si}_{(s)} \rightarrow \text{SiF}_4_{(g)}$$

However this reaction proceeds slowly at room temperature with a reaction rate constant of only $\approx 10^{-5}$ (24), but the reaction rate increases with a rise in pressure and temperature.

Coburn (13) have observed that XeF$_2$ gas reacts with silicon four times faster under the same conditions (pressure and temperature) than F$_2$ gas. This is due to a higher rate of absorption of atomic fluorine species when XeF$_2$ is used. XeF$_2$ chemisorbs on silicon surfaces dissociatively, with Xe being desorbed and leaving greater F$^*$ radical concentrations available for the reaction. Flamm (32) has shown that reactions between fluorine and silicon are rate limited by the reactions of impact ions weakening the Si-Si bond and permitting the reactive species to be directly chemisorbed which would otherwise be a slow process(Fig. 3.1).

Flamm states that the rate determining step is the surface formation of :SiF$_2$ which is released by atomic impact on the silicon surface. Flamm has estimated the kinetic mechanisms for the interaction between F atoms and a solid surface of Si and SiO$_2$. He states that the F atom - silicon reaction alone accounts for the etch rates in plasmas at a few tenths of a torr pressure.
Etching SiO$_2$ in a CF$_4$ plasma using a barrel reactor produces a extremely low etch rate because of the absence of ion impact. Some etching processes will occur from the F$^*$ radicals and CF$_3$$^*$ radicals produced. However, silicon reacts much faster with F$^*$ than CF$_3$$^*$ radicals because CF$_3$$^*$ radicals have a very low reaction rate constant with Si of $10^{-5}$. Thus selectivities greater than 40:1 for Si to SiO$_2$ in a barrel reactor may be achieved. Etching Si and SiO$_2$ in a CF$_4$ plasma using a planar reactor introduces ions and free radicals both of which are capable of etching the solid samples.
Fig. 3.1  When F atoms reacting with the surface, a small fraction attack underlying bonds to liberate SiF$_2$ (Ia), while the major reaction pathway proceeds with fluorinated moieties (Ib) which are saturated through a series of additions (II, III) before desorbing as SiF$_2$. Experiment shows that the fractions of product desorbing as SiF$_2$ (Ia) and SiF$_4$ (III) are temperature independent, which suggests that (Ia) and (Ib) are two pathways of a single reaction.
3.4.2 Ion Impact Etching

The main component of the electron fragmentation of CF$_4$ will be CF$_3^+$ because of the stable planar structure of the ion. Thus CF$_4^+$ will not exist because of the high CF$_3^+$ stability. Coburn (13) extracted and analysed ions from a CF$_4$ plasma and observed the largest peak for CF$_3^+$ with some ionized dimer products.

In the presence of a positive ion sheath at the work surface, the ions will obtain kinetic energy and bombard the surface at a predominantly normal inclination. This would result in anisotropic etching as shown in Fig. 3.2 (a). The ion induces reaction on impact, provided the reaction is rapid and the fragmented free radicals produced are consumed by the reaction in the bombardment vicinity. Free radicals produced in plasmas are not influenced by the dark space field and, in sufficient concentration, will etch laterally, that is isotropic etching with characteristic undercutting of the mask area as shown in Fig. 3.2 (b).

An isotropic etching, such as in substrate etching with certain wet chemicals, can be defined by the relation $A = 1$ when $x = d$, where $(A = d/x)$ and a totally anisotropic etch is defined as $A = \infty$, which is no undercut or line width loss ($x = 0$). However, in plasma etching the etched characteristics are not purely isotropic or anisotropic profiles. For example, in a barrel reactor using a CF$_4$ plasma, silicon is etched in a isotropic-like profile, (A just a little above unity).
When a process shows a value of $A$ larger than 1 it is called an anisotropic process, since there is a large increase in the vertical etch component compared with the horizontal etch components of silicon and other semiconductor materials. Almost pure anisotropic etching can be obtained when etching proceeds by ion bombardment inducing surface reactions without any independent free radical contribution. But a process such as the etching of silicon layers using fluorinated gas in a planar reactor can achieve very high values of $A$, ($A > 1000$). During etching ion bombardment can also sputter away from the substrate surface any polymer or resist deposits which may redeposit onto the sidewalls of the etched profile, thus reducing the free radical lateral etching component (17).

With any plasma process the type of etch profile will depend on the relative contributions from free radicals and ion impact. If the etching process is totally ion impact dependent then a change in free radical concentration should not affect the etching. In SF$_6$ plasma etching of silicon in a planar reactor, the etching is both free radical and ion impact enhanced. Addition of O$_2$ to a SF$_6$ plasma increases the free radical $F^*$ concentration, and makes the etching more isotropic. Addition of H$_2$ to a SF$_6$ plasma will reduce the free radical $F^*$ concentration by H-F formation thus making etching more anisotropic. Etching silicon in SF$_6$/H$_2$, or gases of high carbon to fluorine ratio will be slow polymer deposits being removed solely by ion bombardment. Etching silicon oxide in a CF$_4$ or
SF₆ plasma using a planar reactor will proceed with a high degree of anisotropy since etching is enhanced by surface ion bombardment and the free radical reaction rate constant is low.
Fig. 3.2 (a) anisotropic etching; (b) isotropic etching.
3.4.3 Polymer formation in etching process

The effect on the silicon etch rate from a fluorocarbon plasma can be considered as a balance between etching and polymer formation at the wafer surface depending on the C : F ratio of the gas. The polymer can be sputtered by ion bombardment leaving the wafer surface free to be attacked by fluorinated radicals. The effect of sputtering polymer away by increasing the negative bias potential on the sample.

The electrode potentials developed in plasma reactors (11,15) can be as high as 100 to 1000 volts peak to peak value. At a high plasma to wafer potential, i.e. high ion bombardment energies.

Coburn and Winters (13), using a CF$_4$ plasma in a planar etcher, observed the silicon decrease in etch rate with O$_2$ reductions and H$_2$ additions to a CF$_4$ plasma; at the same time the etch profile became more anisotropic. The silicon etch rate on the r.f. electrode in plasma increased as the negative bias to ground on the r.f. electrode increased, coinciding with an increase in anisotropic profile of the etched silicon. The reaction rate between CF$_3^+$ react ion and Si is low and a thin carbonaceous film is formed on Si$_x$ surfacet which may inhibit further etching. From p.41, the products CO, CO$_2$ and COF$_2$ will be formed when CF$_3^+$ ion is reacted with SiO$_2$ surface, no carbonaceous film is formed. Thus clean SiO$_2$ surface is exposed to the etchant (such as CF$_3^+$ ion and F$^*$ radical) and the etch rate of SiO$_2$ is relatively increased, the selectivity between Si and
SiO$_2$ is obviously decreased. Fig. 3.3(a,b,c) summarises Coburn and Winters' results for the conditions affecting etching and polymer formation.

Fig. 3.3a  Polymer formation related to O$_2$ additions to CF$_4$ plasma and total pressure at constant d.c. bias voltage.

Note: A is polymer formation area
      B is isotropic etching area
Fig. 3.3b  Polymer formation related to $O_2$ additions to CF$_4$ plasma and d.c. bias voltage at constant total pressure.

Fig. 3.3c  Polymer formation related to d.c. bias voltage and total pressure at constant $O_2$ additions to CF$_4$ plasma.
3.5 Carbon Containing Mixed Halogens (CF_xX_n) Plasmas

Fluorine is the most electronegative halogen with the strongest bond to carbon: C-F > C-Cl > C-Br > C-I. In the plasma inelastic electron collisions with CF_xX_n molecules will excite, ionize and rupture bonds. The central carbon atom CF_xX_n will tend to hold onto the fluorine and release X_n during inelastic electron collisions.

\[ \text{CF}_x\text{X}_n \longrightarrow \text{CF}_x^+ + \text{X}_n^+ \quad \text{(bond rupture)} \]

\[ \text{CF}_x\text{X}_n \longrightarrow \text{CF}_x^+ + \text{X}_n^+ \quad \text{(ionization)} \]

The CF_x^+ radical may polymerize, and this will reduce the effect of fluorine chemistry in the plasma and the X_n chemistry will dominate, depending on the level of concentration.

Paraszczak and Hatsakis (34) have compared the effects of etching silicon when oxygen is added to a CF_4 and CF_2Cl_2 plasmas. Using emission spectroscopy they observed overall yields of F and F_2 concentrations in the CF_2Cl_2 plasma to be much lower than observed in the CF_4 plasma. The etching rate for CF_2Cl_2 was slower than CF_4 for the same amount of O_2 present. In every case the CF_2Cl_2 produced a more anisotropic etching profile. With no oxygen present the CF_2Cl_2 gave a low etch rate but a highly anisotropic profile. The etching of silicon in CF_2Cl_2 appears to be mainly by chlorine ions bombarding the surface, since the bond energy of C-F > C-Cl, chlorine is likely produced, with C_2F_4 and COF_2 (O_2 addition) being stable products.
Chapter 4: Polarized Laser Beam Irradiation

4.1 Theories For Polarized Laser Induced Periodic Structures

The process of periodic structure formation has two main stages:

1. Interference pattern formation at the surface.
2. Energy absorbed by the polymer surface.

There are several theories in the literature to postulate the formation of a periodic pattern on polymer surfaces by laser irradiation. First, in terms of the conditions of surface electromagnetic waves (SEW) existence, they should satisfy: (i) Maxwell's equations; (ii) Ordinary boundary conditions; (iii) The condition where $n << k$, $n$ is the index of refraction and $k$ is the extinction coefficient of the material for the laser irradiation. It has to be fulfilled in order that the amplitude of the wave to decrease exponentially in the two directions normal to the interface. For Kapton type polyimide, $n$ and $k$ are estimated according to the data (51) to be $n = 1.7$ and $k = 0.6$ for $\lambda = 266$ nm. Thus polymers do not meet the conditions for SEW. The laser intensity modulation at the polymer surface is due to interference of the incident beam scattered along the surface radiation at the initial stage and later scattered with generated surface waveguide modes. The periodic pattern develops with every consecutive pulse. The amplitude of the periodic structure (the distance between the minimum point and the maximum
point) is about 60 nm for 2 min exposure. After 10 min exposure the depth of the ripples increased to 120 nm. This proves the process is self-organizing. However, a polymer surface periodic structure can couple waveguide modes with the same polarization only, (not with the orthogonal polarization), thereby amplifying the waveguide modes in a particular direction.

The energy absorption on polymer surface is based on the relationship between the intensities of incident light ($I_0$) and transmitted light ($I$).

$$\frac{I}{I_0} = \exp(-\alpha \cdot d)$$

where $\alpha$ is the absorption coefficient; $d$ is the depth of penetration.

For PMDA-ODA type polyimide film: $\alpha = 3 \times 10^5$ cm$^{-1}$

$$d = \frac{1}{\alpha} = 3.33 \times 10^{-6} \text{ cm}$$

= 0.03 $\mu$m

= 30 nm
Fig. 4.1  Light scattering from the polymer surface.

Fig. 4.2  Interference between the incident beam and the scattered light.
Fig. 4.3  The most regular periodic structure is the waveguide modes have polarization vector parallel to the polarization vector of the incident laser radiation.
4.2 Process Requirement for Periodic Structure Formation

For the generation of periodic structures the laser radiation must satisfy the following conditions:

1. Fully plane polarized.

2. The fluence has to be large enough to cause polymer surface melting, but it should be below the ablation threshold of the polymer we use.

The most regular periodic structures are those whose wave-guide modes have polarization parallel to the polarization of the incident radiation, and the same periodic structure is formed by the interference between the incident beam \( I_o \) and the waveguide mode of the same periodic structure, \( I_{WM} \).

\[
I_{\text{max}} = I_o + I_{WM} + 2(I_o I_{WM})^{1/2} ;
\]
\[
I_{\text{min}} = I_o + I_{WM} - 2(I_o I_{WM})^{1/2}
\]

When \( I_o = I_{WM} = I \); then \( I_{\text{max}} = 4I \) & \( I_{\text{min}} = 0 \)

With the fourth harmonic mode and a wavelength of 266 nm laser beam the periodicity obtained ranges from 220 to 320 nm, that is corresponding to the wavelength of the laser beam. The periodicity of the surface pattern depends on the wavelength of the incident laser radiation \( \lambda \), angle between the interfering
waves $\phi$, and the refractive index of the material, $n$:

$$\Lambda = \frac{\lambda}{n \sin \phi}$$

A well-defined periodic pattern is generated when the angle of the incidence is lower than $70^\circ$. 
4.3 The dielectric periodic waveguide

A periodic dielectric waveguide in which the periodicity is due to a corrugation of one of the interfaces as shown in Fig. 4.4. The corrugation is described by $\Delta \varepsilon(x, y, z) = \varepsilon_0 \Delta n^2(x, y, z)$. Since $\Delta n^2(x, y, z)$ is a scalar, the corrugation couples only TE to TE modes and TM to TM modes, but not TE to TM. The basic requirement is

$$\beta_k - \beta_m = \frac{2\pi}{\Lambda}$$  \hspace{1cm} (4.3-1)

for some mode $m$ with propagation constant $\beta_m$ and some integer $l$. When the condition (4.3-1) is satisfied, the $k$th mode and $m$th mode are resonantly coupled via the $l$th Fourier component of the periodic perturbation $\Delta \varepsilon(x, y, z)$.

Consider the square wave corrugation of Fig. 4.4. In this case, the dielectric perturbation $\Delta \varepsilon(x, z)$ can be expressed in

$$\Delta \varepsilon(x,z) = \Delta \varepsilon(x)[f(z) + 1]/2$$  \hspace{1cm} (4.3-2)

where $f(z)$ is the square-wave function .

where $\Delta \varepsilon(x) = \varepsilon_0(n_1^2 - n_2^2)$,  \hspace{1cm} -a \leq x \leq 0  \hspace{1cm} (4.3-3)

$0$ \hspace{1cm} otherwise
Fig. 4.4 The corrugated periodic waveguide.
Chapter 5: Experimental

5.1 Baseline Process on Wafer

OCG Company Probimide 114 (PMDA-ODA Polyamic acid precursor) as received from the manufacturer, the polyamic acid is soluble in strong basic solvents such as NMP (N-Methylpyrrolidone). To obtain good adhesion between the silicon wafer and polyamic acid coating, the wafer was put in HMDS (Hexamethyldisilazane) vapor in an oven to prime a thin silylated layer on the surface or pre-spun with 0.05 % DuPont VM651 (amino propyltriethoxy silane) or other organosilane as adhesion promoter in 95/5 (v/v) methanol/H2O (Fig. 5.2). The polyamic acid solution were spun in a class 1000 clean room environment at spin speeds of 5000 - 5500 rpm to achieve 1.80 - 2.25 µm film thickness. The coating must be prebaked to remove solvent and in the process the polyamic acid coating is partially imidized. The degree of this bake determines the conditions for etching and stripping. Films were soft-baked 30 minutes at 90°C ± 5°C while held horizontally in a forced air oven. Films were then hard-baked at 250°C in nitrogen atmosphere in order to complete the imidization to obtain the full film properties. The final curing time was about 30 min.

Polyimide films from Probimide 114 are prepared from the polycondensation reaction between a pyromellitic dianhydride and oxydianiline. (Fig. 5.1). Since polyimides are not soluble in most common solvents, they are usually applied in the form of
their precursors, the polyamic acids. The solution of the polyamic acid is applied to the substrate and thermally cured to form the polyimide film.

\[
\begin{align*}
\text{PMDA} & \quad + \quad \text{ODA} \\
\xrightarrow{\text{Ar} = \text{C}_6\text{H}_5} & \\
\text{Polyamic Acid}
\end{align*}
\]

Fig. 5.1a Polycondensation reaction between a PMDA and ODA.  
(Step 1)
Fig. 5.1b Polycondensation reaction between a PMDA and ODA. (Step 2)
Fig. 5.2 Proposed mechanism of adhesion promotion by silane coupling agents. The silane compounds form bridges between the silicon surface and polyimide (Sequence a-d).
5.2 Laser processing on polymer surface

A Spectra-Physics Quanta-Ray GCR-4 Nd:YAG laser was used at its fourth harmonic mode with a wavelength of 266 nm. (Fig.5.3) A linear periodic structure is created simply by exposing the polymer surface to a polarized laser radiation, and only one beam is introduced, and without any optical components, like a mask or scanning device. The experiment was carried out in a extremely small fluence condition, far below the photoablation threshold. For dot array patterns the polarized beam was split into two beams, with a polarization plane orthogonal to each other. These two beams were brought at the same polymer surface areas. The exposures were carried out with a fluence of 4 to 6 mJ.cm⁻² at a repetition rate of 10Hz. The fluence range is far below the fluence of photoablation. The exposures were carried out in atmospheric conditions with more than 1000 5 nsec laser pulses with Q switch modulation. Polymers used are polyimide films (XU 218, Ciba Geigy) and polyamic acid precursor (Probimide 100 and 114, OCG Microelectronic Materials) on silicon substrate. The exposure time for each ripple is between 8 to 10 min. Four ripple patterns can be produced in a 1-inch dia. wafer without interference with each other. The angle of incidence is adjusted to 60°.
Fig. 5.3 Fourth Harmonic Generation (266nm) occurs by generating the second harmonic of the second harmonic of the fundamental output.
5.3 Image transfer process by RIE and Plasma Etching

A 12.5 % diluted solution of polydimethylsiloxane in xylene or toluene was prepared. 2.0 to 3.0 ml of the solution was delivered to the center of a non-spinning 25.4 mm (1 in.) diameter wafer with a positive displacement bellows-type pump. Spinning then progressed until 5000 rpm for 25 seconds. Film was soft-baked at 90°C-100°C for 20 min. to 30 min. in a N₂ purge oven. Finally, the film was hard-baked at 200°C in N₂ atmosphere.

For the image transfer process, the system (Dry Tek DRIE-102) employed in this fabrication was a batch type reactor consisting of five parallel plate electrodes which had an interelectrode spacing of 2.4 cm and electrode area of 1190 cm². RF power at 13.56 MHz was applied on the target electrode which was a water-cooled cathode. The system was pumped by a blower pump aided by a mechanical pump.

The gases used for the reactive ion etching were SF₆, O₂ and C₂ClF₅. From Fig. 5.4 shown the image transfer process to generate quarter-micron structures on silicon or other semiconductor wafer surfaces. Fig. 5.4a shows a thin film of polydimethylsiloxane or other similar polysiloxane layer on top of the periodic structure by filling the valleys of the structures. By back-etching of the polydimethylsiloxane except those filling the volume of the valley-structures, using CF₄ or SF₆ with around 8% O₂ as etching gases and other appropriate plasma process
parameters to etch the polysiloxane layer with different times of exposure in order to get different expose areas or linewidths of polyimide surface. (Fig. 5.4b). Then, by applying O₂ RIE the exposed polyimide is etched with careful feature-size and anisotropic control. Based on the selectivity(etch ratio) between polyimide and polydimethylsiloxane layers, the time can be estimated the time to etch away the desired depth until silicon is exposed. (Fig. 5.4c). Followed by using SF₆ and C₂ClF₅ etching gases to etch the exposed silicon areas. (Fig. 5.4d). During the reactive ion etching of silicon, as inhibitor film was formed on the surface and the sidewall of the silicon trench areas. This interferes badly with further etching of silicon and deep trench formation. However, using small amount of oxygen plasma to oxidize the plasma polymerized inhibitor film to generate the volatile product can enhance the silicon etching. Owing to the trench width and the adhesion properties of plasma polymer film on silicon wafer, it is difficult to remove all the residue plasma deposits from the patterned silicon wafer. Finally, (Fig. 5.4e) after straight O₂ plasma ashing the patterned wafer is placed in the H₂SO₄/H₂O₂ to remove the excess polyimide on the silicon wafer. After the silicon wafer was dried in N₂ atmosphere, the wafer was then placed into the HF/NH₄F for the final cleaning process. The purpose of HF/NH₄F was to remove the silicon oxide layer formed by oxygen plasma.
(a) Polysiloxane

(b) ~ 250 nm

(c) Oxygen RIE

(d) SF6/C2ClF3

(e) O2 plasma

HF/NH4F

Fig. 5.4 Image transfer process by Reactive Ion Etching
Chapter 6: Results and Discussion

6.1 Atomic Force Micrography

Well defined, non-disturbed, periodic patterns are generated when the angle of incident laser beam is lower than 70°. Due to various factors the ripple spacing can vary within a range of about 30 nm in a single experiment. (9)

As shown in Fig. 6.1, the three-dimensional view of an AFM micrograph, the surface of a ripple structure is cylindrical with circular or elliptical cross section for poly(ethylene terephthalate). The response of the material is not linear to the sinusoidal changing of the intensity of laser radiation, resulting in interference of incident beam and the scattered light. The surface shape may due to the surface tension of the melted polymer and the lateral gradient of viscosity generated by the temperature gradient.
Fig. 6.1 AFM three-dimensional view of linear periodic structure on Poly(ethylene terephthalate) surface after 5 minutes exposure with 5 mJ/cm².
6.2 Scanning Electron Micrography

Fig. 6.2 shows SEM micrographs of the periodic linear structure made on cured Probimide 114 films. There is a slight difference in the periodic structures depending on whether the films were unstretched, or stretched uniaxially or biaxially. So, the mutual orientation between the plane of polarization and the direction of stretching polymer films does not influence the surface profile of the ripple. However, some ripples were split into branched ripples. The time of exposure under a fluence of 4 mJ/cm² is 5 min. The angle of incidence was 45°.

Fig. 6.2a shows SEM micrographs of the periodic linear structure of polyimide with 75,000X magnification. The width of each ripple line is about 250 nm. The energy density is 5 mJ/cm² and the time of exposure is 8 min. The angle of incidence was 45°.

As shown in Fig. 6.3, the periodic trench profiles were highly anisotropic after image transfer by RIE. It is evident that the polymer actually causes the deposition of a polymer thin film on the sidewall surface which inhibits the lateral etching.

The image transfer process was based on Fig. 5.4(a-e). Fig. 6.3 was fabricated under the following conditions:
From (a) to (b) : To etch the poly(siloxane), SF₆ gas was used. The gas flowrate was kept constant at 40 sccm. The RF power at 500W (0.42 W/cm²), chamber pressure at 60 mtorr, temperature of cathode coverplate at 15°C and d.c. bias of 120V. The etch rate in this etching gas system was found to be 30 nm/min (300Å/min). The period of etching was 5 min.
Polysiloxane could be removed isotropically until the peak of polyimide periodic structure was exposed. From (b) to (c): The polyimide etch rate was measured earlier at 700Å/min. The etching gas used was O₂ and the gas flowrate was kept at 40 sccm. The RF power was 500W (0.42W/cm²), the chamber pressure at 60 mtorr, the temperature of electrode kept at 20°C and d.c. bias was adjusted to -125V. After soft and hard baking of Probimide 114 negative resist, the thickness was 1.80 μm for O₂-RIE. The period of O₂-RIE was estimated to be 25 min. From (c) to (d): In order to etch the silicon, a mixture of SF₆ and C₂ClF₅ was used. The etch rate of Si and poly(siloxane) and the selectivity were found to be dependent upon the C₂ClF₅ content and the system pressure. The flow-rate of SF₆ and C₂ClF₅ gases were 25 sccm and 60 sccm respectively. A small amount of O₂ was added in order to eliminate the carbonaceous film during RIE. The flowrate of O₂ was around 3.0 sccm. The RF power at 540W (0.46W/cm²), the chamber pressure at 55 mtorr, the temperature of electrode at 18°C and d.c. bias was kept at -130V. Finally, the duration of etching Si<100> was 1 hr. From (d) to (e): After etching of silicon, by straight O₂ plasma ashing followed by CARO process (treated with H₂SO₄/H₂O₂) to remove the excess polyimide after etching, but the plasma deposit on the trench surface and sidewall cannot be removed by CARO process and buffered oxide etcher (HF/NH₄F mixture). Finally, the patterned wafer should be cleaned and dried by rinsing with deionized water and blown under N₂ atmosphere.
Fig. 6.3a shows an SEM micrograph of surface damage pattern of quarter-micron periodic structure after SF$_6$-RIE. The flow-rate of SF$_6$ and C$_2$ClF$_5$ were both 25 sccm. The RF power density was kept at 0.43W/cm$^2$, the chamber pressure at 62 mtorr, the temperature of electrode kept at 20°C and d.c. bias of -80V. The duration of etching Si<110> wafer for Fig. 6.3a was 15 min.

Fig. 6.3b shows an SEM micrograph of surface profile after overetching of periodic structure. From the surface morphology on Si<100> wafer, the ripple pattern can be seen with a high isotropic profile or overetched surface. The gas used was SF$_6$ without C$_2$ClF$_5$, the flow-rate of SF$_6$ was 30 sccm, the chamber pressure at 85 mtorr, the temperature of electrode at 20°C and d.c. bias of -80V. The duration of etching for Fig. 6.3b was 15 min.

Fig. 6.3c shows an SEM micrograph of structural damage of trench after SF$_6$ RIE treatment. The experimental conditions for etching poly(siloxane) and polyimide were similar to that of Fig. 6.3. For the etching of silicon, the flow-rate of SF$_6$ and C$_2$ClF$_5$ were 25 sccm and 50 sccm respectively. RF power density was kept at 0.46W/cm$^2$, the chamber pressure at 60 mtorr, the temperature of electrode at 18°C and d.c. bias of -120V. The duration of etching for Fig. 6.3c was 30 min.

Fig. 6.3d shows an SEM micrograph of a thin polymer deposit was formed on the silicon surface. The polymer was redeposit after O$_2$-RIE at 90 mtorr chamber pressure, 35 sccm O$_2$ flowrate, power density 0.42W/cm$^2$ and d.c. bias of -90V.

sccm (standard cubic centimetre per minute)
Scanning electron microscope (SEM) observations have been done to investigate the trench shape and surface topography of etched sidewall. Example of SEM micrograph is given in Fig. 6.3. A rough surface for the etched silicon sidewall can be observed. It is generally accepted that there is some polymer-like material forming on the sidewall of the trench structure during RIE process, and it acts as an inhibitor to passivate or protect the features from etching species (13). It is believed that the deposition of polymer-like residue on the trench surface has been caused by carbon and fluorine contamination coming from the interaction between SF₆, C₂ClF₅ and the silicon wafer. In the SF₆/C₂ClF₅ system, the competition between chlorine and fluorine for the active sites on Si surface will determine the Si etch rate. The drop of Si etch rate with C₂ClF₅ flow-rate in Fig. 6.5c can be accounted for by the adsorption of a high concentration of chlorine atoms onto the silicon surface, preventing the occurrence of etching from the attack of excited fluorine atoms. O₂ degrades the polyimide and produces a great number of carbon atoms which consequently cause the formation of polymer-like residue. If a small amount of oxygen (about 8% of the flow-rate of etching gas) is introduced in Si etching, the polymer-like residue again will compete with chlorine, fluorine and oxygen for chemisorption on the silicon surface. On the horizontal Si surface, adsorption of oxygen or polymer residue can be attacked through the reactive ion bombardment. While on the silicon sidewall surface, the removal of sidewall material is not significant at all because of the less directional kinetic energy in this orientation.
Fig. 6.2 A SEM micrograph of a typical periodic linear structure produced by Nd: YAG 4th harmonic generation on polyimide.
Fig. 6.2a A SEM micrograph of a typical periodic linear structure produced by Nd: YAG 4th harmonic generation on polyimide with 75,000 magnification.
Fig. 6.3  Si(100) surface pattern of quarter-micron periodic structure after image transfer by RIE.
Fig. 6.3a  Surface damage pattern of quarter-micron periodic structure after SF6-RIE.
Fig. 6.3b  Si(100) surface profile after overetching of periodic structure.
Fig. 6.3c  Structural damage of trench after RIE.
Fig. 6.3d  Polymer redeposition after plasma etching.
The SEM analysis had three goals. First was to provide information about the trench profile and the thickness and shape of the sidewall passivation material deposited for profile control during trench etching. Second was to provide qualitative information about the composition of the sidewall passivation based on its etch characteristics. Third was to provide a method of assessing the efficacy of trench cleaning for the physical removal of the sidewall passivation material.

Trench etching with C$_2$ClF$_5$ resulted in a composite sidewall passivation material. This was composed of an oxide-like material that could be removed by HF/NH$_4$F (buffered oxide etcher) and a carbonaceous material that required O$_2$ ashing for removal. For Fig. 6.3, the material along the vertical surface of the trench appears to be more silicon-rich, whereas the material around the mask surface appears to be more oxide-like. A potential mechanism consistent with the data can be developed by examining the reactions occurring during the etch. The reactants were SF$_6$, C$_2$ClF$_5$ and O$_2$. The major silicon etchant is the fluorine radical F$^\circ$

$$\alpha F^\circ + \beta Cl^\circ + Si_{surface} \rightarrow SiCl_{\beta}F_\alpha (g)$$

$$1<\alpha<4 \ & \ \beta = 4 - \alpha$$

The SiCl$_{\beta}F_\alpha$ is presumed to be an etch product with a rate of production at the bottom of the trench proportional to the silicon etch rate. This reaction product is unstable and can decompose or react with fluorine or oxygen radicals at the vertical trench sidewall.
\[ \text{SiCl}_\beta F_\lambda + x\text{O}^* \rightarrow \text{SiO}_x (s) \]
\[ \text{SiCl}_\beta F_\lambda + (4 - \alpha)\text{F}^* \rightarrow \text{SiF}_4 \ (g) \]

The reaction with oxygen atom radicals can form an unsaturated (Si-rich) oxide deposit and the reaction with fluorine atoms forms volatile SiF\(_4\). If the oxygen concentration is increased relative to the fluorine concentration, more deposition will occur. Conversely, if the oxygen is depleted, the sidewall passivation layer will not be formed and the trench etching can become isotropic. The reaction(s) which contribute to the deposition of material on the horizontal mask surface can occur without a SiCl\(_\beta\)F\(_\lambda\) intermediate. For example:

\[ \text{SiF}_4 + y\text{O}^* \rightarrow \text{SiO}_y + 4\text{F}^* \]

This reaction could also contribute to the deposition on the vertical and bottom surface, but will be less important as trench etching progresses. The oxygen concentration will be higher near the top of the trench feature and will decrease with the vertical position in the trench because of mass transfer limitations.

As we can see from the SEM micrographs in Fig. 6.3, 6.3a and 6.3c, the etch profile of the periodic structure is strongly dependent upon the ratio between SF\(_6\), C\(_2\)ClF\(_5\) and O\(_2\). Our study shows that etching of silicon trenches depends mainly on the chemical composition of the gas mixtures.

We expect that the presence of carbonaceous material is due to the contamination from both the polymer residue and carbon-containing gas species (C\(_2\)ClF\(_5\)) after plasma process.
This contamination is hardly removable with post-RIE surface treatments such as solvent cleaning, $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2$ treatment, oxygen plasma ashing etc.
6.3 Etch rate experimental results

The etch rates of polyimide, silicon-oxide containing polymer and resist were measured using a Nanometrics™ optical reflection system, and the etch rate of Si under different plasma condition was determined by a surface profilometer. Fig. 6.5 shows the effect of O₂ pressure on the polyimide and PMMA etching rate. PMMA shows a significantly lower etch resistance than that of polyimide under identical RIE conditions. This is due to the aromaticity of the polymer. Fig. 6.5a shows there is a critical flow-rate to affect the etch rate of silicon dioxide. At lower CF₄ flow-rates the products are pumped away more slowly thus the probabilities of both dissociation and recombination reactions are relatively higher. As the flow-rate is raised the products are pumped away faster and result in less recombination of the radicals, so that the reactant gas is less involved in the reaction. The etch rate is maintained in a steady state as the flow-rate is higher than the critical flow-rate. Fig. 6.5b shows that the silicon etch rate is almost independent of the loading effects. Comparing the silicon areas of 5 cm² and 20 cm², only a slight reduction in the etch rate of silicon under RIE mode is found for the larger sample. Fig. 6.5c shows the etch rate of Si was found to be dependent on the ratio of flow-rates and the total pressure of SF₆ and C₂ClF₅ mixture. It is evident that the flow-rates of C₂ClF₅ actually causes the deposition of a thin polymer-like film on the sidewall and the bottom of the trench which inhibits the lateral etching.
Fig. 6.4 Etch rates of polyimide, PMMA resists by Reactive Ion Etching (RIE) at 13.56 MHz, 0.42 watts/cm² and dc bias of -130V. PMMA shows a significantly lower etch resistance. Aromatic polyimide has exhibit a higher etch resistance.
Fig. 6.5a  SiO$_2$ Etch Rate vs CF$_4$ flow rate at 100 Watts power and 0.1 torr pressure
Fig 6.5b Silicon etch rate in RIE vs. exposed silicon wafer area to the CF$_4$ with 8% O$_2$ plasma
Fig. 6.5c  Etch rates of Silicon against $\text{C}_2\text{ClF}_5$ flowrate at pressures of 65 and 80 mtorr
6.4 X-ray Photoelectron Spectroscopy

XPS has shown that samples 1 and 2 which were treated with low SF$_6$ to C$_2$ClF$_5$ ratios incorporate fluorine into the polymer backbone as a mixture of CF$_x$ type and chlorinated compounds. From XPS data indicated that the major peak centered at 688.2 eV in F(1s) spectrum is representative of C-F covalent bond in the polymer matrix (9). Thus, at high SF$_6$ to C$_2$ClF$_5$ ratio like sample 3, SF$_x$ bonds in the sample predominate increasing the etch susceptibility which infers the apparent increase in etch rate. However, there were no Cl (2p3) signals in the XPS spectra and O$_2$ plasma followed by CARO process removed most of the fluorinated deposit, if there is a small amount of fluorinated deposit left, this probably bound to the silicon from the binding energy $E_b$(F(1s)) = 687.3 eV and consequently becomes 'less oxidized' which means the oxygen is less bound to the silicon in order to form a SiO$_x$ layer. Back to sample 2, it shows a higher fluorine content on polyimide surfaces when compared to identical percent C$_2$ClF$_5$ in SF$_6$/C$_2$ClF$_5$ mixture, since the total fluorinated gas flowrate implied more fluorine atoms contribution in plasma process(10).
<table>
<thead>
<tr>
<th>Sample Wafer</th>
<th>Gas (Flowrate)</th>
<th>Reactor Pressure</th>
<th>Power Density</th>
<th>Exposure Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1 (S1)</td>
<td>SF6 25 sccm C2ClF5 60 sccm</td>
<td>70 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>30 min.</td>
</tr>
<tr>
<td></td>
<td>SF6 40 sccm O2 3.2 sccm</td>
<td>70 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>4 min.</td>
</tr>
<tr>
<td></td>
<td>O2 35 sccm</td>
<td>60 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>15 min.</td>
</tr>
<tr>
<td>Sample 2 (S2)</td>
<td>SF6 25 sccm C2ClF5 70 sccm</td>
<td>65 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>SF6 40 sccm O2 3.2 sccm</td>
<td>65 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>8 min.</td>
</tr>
<tr>
<td></td>
<td>O2 40 sccm</td>
<td>60 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>30 min.</td>
</tr>
<tr>
<td>Sample 3 (S3)</td>
<td>SF6 25 sccm C2ClF5 25 sccm</td>
<td>60 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>2 hours</td>
</tr>
<tr>
<td></td>
<td>SF6 40 sccm O2 3.2 sccm</td>
<td>60 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>8 min.</td>
</tr>
<tr>
<td></td>
<td>O2 30 sccm</td>
<td>55 mtorr</td>
<td>0.46 W/Sq. cm</td>
<td>30 min.</td>
</tr>
</tbody>
</table>

Fig. 6.6 Sample Wafers for ESCA analysis
<table>
<thead>
<tr>
<th>Sample Wafer</th>
<th>Si (2p)</th>
<th>C (1s)</th>
<th>F (1s)</th>
<th>O (1s)</th>
<th>N (1s)</th>
<th>Cl (2p3)</th>
<th>S (2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 (S1)</td>
<td>99.5 eV</td>
<td>285.3 eV</td>
<td>686.5 eV</td>
<td>532.8 eV</td>
<td>401.3 eV</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>Sample 2 (S2)</td>
<td>99.3 eV</td>
<td>285.0 eV</td>
<td>688.2 eV</td>
<td>532.6 eV</td>
<td>400.7 eV</td>
<td>201.3 eV</td>
<td>No data</td>
</tr>
<tr>
<td>Sample 3 (S3)</td>
<td>99.5 eV</td>
<td>285.7 eV</td>
<td>687.3 eV</td>
<td>533.0 eV</td>
<td>402.4 eV</td>
<td>No data</td>
<td>178.0 eV</td>
</tr>
</tbody>
</table>

Fig. 6.7 ESCA data with different gas composition of plasma treatment
Fig. 6.8 XPS spectrum of Sample 1.
Fig 6.8a XPS spectrum of Si(2p) peak.
Fig 6.8b  XPS spectrum of Si(2s) peak.
Fig 6.8f XPS spectrum of O(1s) peak.
Fig 6.8g  XPS spectrum of F(1s) peak.
Fig 6.9a: XPS spectrum of Si(2p) peak.
Fig 6.9b XPS spectrum of Si(2s) peak.
Fig 6.9c  XPS spectrum of Cl(2ps) peak.
Fig 6.9e XPS spectrum of N(1s) peak.
Fig. 6.9f XPS spectrum of O(1s) peak.
Fig 6.9g XPS spectrum of F(1s) peak.
Fig 6.10 XPS spectrum of Sample 3.
Fig 6.10a XPS spectrum of Si(2p) peak.
Fig 6.10c XPS spectrum of S(2p) peak.
Fig 6.10d  XPS spectrum of C(1s) peak.
Fig 6.10e  XPS spectrum of N(1s) peak.
Fig 6.10f  XPS spectrum of O(1s) peak.
Fig. 6.10g XPS spectrum of F(1s) peak.
Chapter 7: Conclusion

Silicon (Si<100>) quarter-micron structures can be fabricated in periodic trench form by polarized laser irradiation on polyimide surfaces, using polydimethylsiloxane as a filler on the periodic structure to form a bilevel polymer layer and RF controlled reactive ion etching of the silicon substrate combined with plasma "ashing" and CARO process. Observation by scanning electron microscopy confirms that the width of each etched line is about 200 nm, the spacing between them is about 100 nm and the depth of each trench is about 160 nm. XPS and SEM spectra allowed examination of residue layers impurities as well as surface roughening effects and charge buildup damage. This technique without using photomask and other scanning devices would make it possible to fabricate silicon quantum devices as well as to fabricate conventional integrated circuit and nano-line features on the same silicon chip, which may lead to their application in integrated optoelectronic devices.
REFERENCE

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