Chapter 1

Low pressure rf plasmas

The advent of plasma physics, although with a long pre-history including Franklin's experiments with lightning, can probably be said to have begun in 1879 with Crooke's demonstration of the magnetic deflection of cathode rays, which he presciently described as "the fourth state of matter" (Penning (1957), Introduction). By the turn of the century much of the early parameterisation of plasmas had been accomplished by a group at Cavendish which included such luminaries as J.J Thompson, E. Rutherford and J.S Townsend. In the 1920s Langmuir published much of the early theory on the "discharge of arcs", and in 1929 Tonks and Langmuir coined the term plasma to describe the collective oscillation of electrons, although with the vagaries of fashion it did not come into common usage until about the 1950's. Much effort has concentrated on the development and understanding of hot, magnetically confined plasmas for fusion since the 1940s. However, it is not until about two decades ago that the technological application of low pressure rf plasmas for materials processing was realised.

Despite a long history many of the physical processes sustaining rf plasmas is poorly understood, particularly in the complex geometries used in technological applications today. Processing applications require precise control over the plasma, particularly as micro-structures become smaller and more complex. To continue advancing these technologies it is therefore essential to fully understand the physical processes driving the plasma rather than to rely on an empirical knowledge of the behavioural dependence on various input parameters. Plasmas involve complex interactions between charged and neutral particles, the self-fields of the charged particles and the applied fields as well as chemical and surface reactions. Measurements are difficult to make and the results are often difficult to interpret, particularly when complicated by hysteresis effects and unreproducability. Much of the effort in understanding the basic physical processes in plasmas has therefore been carried out in simplified systems, ignoring the complex geometry of industrial machines. Even so results have been contradictory and in a recent venture (Hargis *et al* (1994)) six similar GEC reference cells were manufactured and sent to several different labs in the USA, in order to determine the congruence of the results. Agreement between machines for

1.1.1 Etching

Etching processes today are typically carried out in the presence of reactive gases, and hence are known as Reactive ion etching (RIE). RIE is believed to occur by two mechanisms (1) physical removal of the surface material by high energy ions, as in conventional sputter etching and (2) by chemical reactions of neutral radicals with the surface atoms to form volatile molecules which can then evaporate from the substrate surface. Bombardment by ions also plays a rôle in this process, by accelerating desorption of the molecule. The second process is much more efficient than the first and is believed to be the dominant process taking place in RIE, provided greater numbers of neutrals than ions are present at the substrate surface. RIE therefore requires lower ion energies than sputtering, reducing the risk of damaging the device. However it does require the use of volatile and often toxic gases.

The first process obviously depends on the energy with which ions hit the substrate surface, however recent work indicates that rates in RIE are also directly proportional to the flux of energy to the substrate. This seems to be independent of the type of ions arriving at the substrate (for example, when etching SiO_2 with SF_6 a certain percentage of Ar can be introduced) provided there is a sufficient supply of neutrals (in this case F radicals). This suggests that a certain activation energy is required in order for a chemical reaction between the radical and neutral surface atoms to take place. Thus for both physical and chemical etching processes the arrival energy of ions at the surface is important in determining the rate at which etching occurs. (Austin *et al* (1991)).

Neutrals arriving at the surface will have fairly small, undirected energies, since they are unaffected by the electric fields in the discharge. Hence chemical etching should be a relatively isotropic process, unlike sputter etching which is carried out by ions which

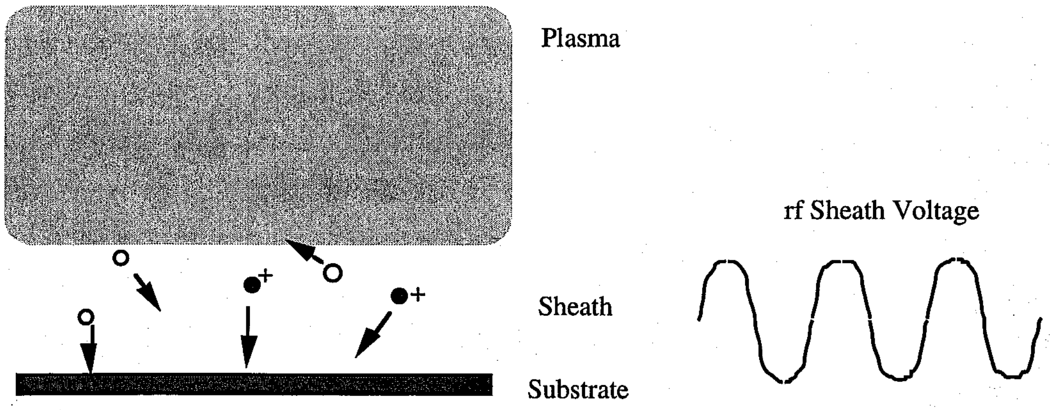

Figure 1.1 Schematic of ion and neutral motion through the rf sheath

have very anisotropic (perpendicular to the surface) distributions due to the large average fields in the region between the bulk plasma and the biased wafer (known as the sheath region). Although neutrals can gain a small average drift velocity through charge-exchange interactions in the sheath, the average bombardment energy of the neutrals is much smaller than the ions. It would therefore appear that RIE should occur equally favourably in all directions, which would make deep, straight-sided trenches extremely difficult to produce. However two phenomena occur which favourably influence anisotropic etching – firstly the ions, which provide the activation energy for chemical etching to occur, impact mainly on the horizontal surfaces; secondly, surfaces which are not directly bombarded by ions form a passivation layer, caused by chemical bonding of neutrals from the plasma with the surface atoms, which is not easily etched and so acts as a sort of secondary mask (Oehrlein *et al* (1990)).

This layer will also appear on the horizontal surface of the substrate if the bombarding ions are insufficiently energetic to remove it, and so for etching to occur the average sheath voltage must exceed a critical value. This is generally produced by creating a negative dc bias at the wafer surface. Once the critical voltage is exceeded, etching rates appear to be linearly dependent on bias voltage, until saturation in the etching rate is reached (Perry (1994), Tadokoro (1989)). Saturation indicates that the etching rate is limited by the availability of the etchant species, rather than the energy flux at the surface. A limitation on the bias voltage is that very large ion energies can cause electrical and structural defects, resulting in degradation of the performance of the device (Austin *et al* (1991), and references therein).

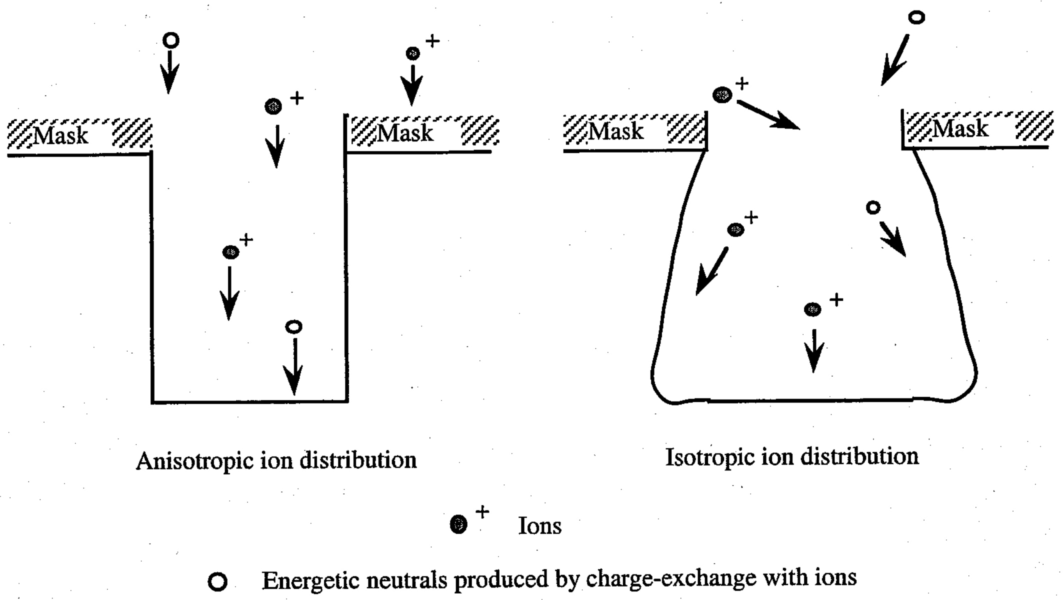

Figure 1.2 Schematic of the effect of the ion angular distribution on the directionality of the etching.

As previously mentioned, the anisotropy of the ion distribution is important, with ions trajectories perpendicular to the surface being the ideal. However elastic collisions with neutrals in the sheath direct the ion trajectories away from the perpendicular, resulting in a distribution of impact angles at the surface. The more collisions the broader the angular distribution, and so the angular distribution is inversely related to the ion mean free path, which to first order depends on the gas pressure. Large angular distributions can result in undercutting of the surface mask on a device, and produce sloped side walls, as shown schematically in Figure 1.2. Ions can also undergo charge exchange interactions with neutrals, in which the an electron is transferred from the neutral to the ion, resulting in a (nearly) stationary ion and a fast neutral. This can substantially reduce the average ion energy at the substrate surface, particularly when ions make multiple charge exchange collisions while traversing the sheath.

To characterise etching performance it is therefore important to have a knowledge of both the ion energy and angular distributions (IED and IAD) at the surface.

1.1.2 Deposition

In deposition the plasma again acts as a source of the reactive neutrals and ion species. Ions can sometimes play a part in reactions at the surface, and in the gas phase can be involved in the production of neutral radicals through collisional processes. In general it is desirable to keep ion energies as low as possible, otherwise etching tends to compete unfavourably with deposition. In some cases, however, it is desirable to have a small bias voltage, since this can help ensure a strongly bonded film. Substrate biases have also been found to be useful in the synthesis of cubic boron nitride films, by preventing the formation of (unwanted) hexagonal boron nitride (Ichiki *et al* (1994)).

1.2 Plasma Reactors

Radiofrequency (rf) and microwave (mw) plasmas are widely used in fabrication of micro-electronic devices, and in modification of surface materials. Typically rf plasmas are operated at 13.56 MHz, while mw sources are run at 2.45 GHz – both of these frequencies represent industrial standards: the rf from radio transmitters and mw from microwave ovens.

Broadly speaking rf plasmas can be categorised as either capacitive or inductive discharges, so called because of their electrical characteristics. Capacitive, or E-type, discharges are generally associated with unmagnetised systems in which the electrodes are in direct electrical contact with the plasma, and the fields are due to the time-varying voltage applied across the electrodes. Inductive, or H-type, discharges are formed when the fields in the plasma are induced by a changing magnetic flux and generally occur in systems in which power is applied to the system via an antenna. However discharge physics is complex and plasmas can often be a mixture of both modes.

For processing applications there are a few important characteristics that the reactor must display:

1) Uniformity – the plasma must be uniform across the processing surface (ie., the entire wafer or series of wafers), so that each devices undergoes the same degree of processing to obtain the correct profile.

2) Stability and reproducibility – the plasma must be stable during the whole processing period (from minutes to hours), to obtain the correct etched profile and must behave in the same fashion every time it is turned on.

3) Controllability – it is useful for parameters such as the plasma density, and the potential across the sheath to be separable since this allows conditions at the wafer surface to be optimised for whatever process is taking place there.

1.2.1 Parallel Plate Reactors

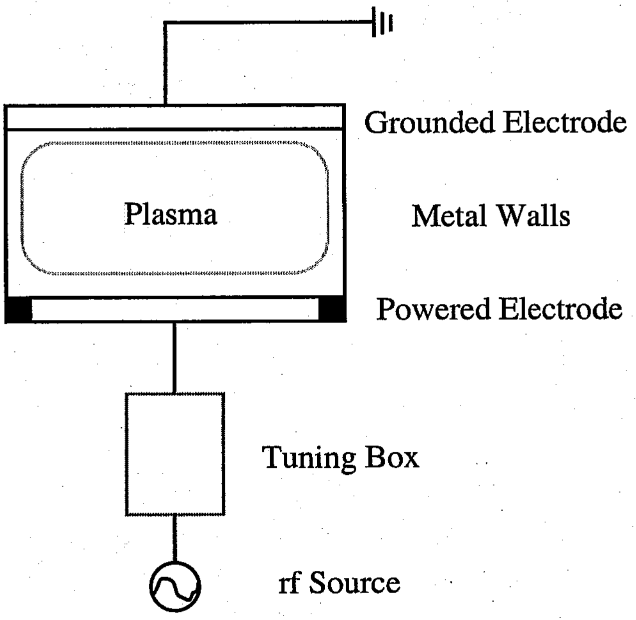

Figure 1.3 Schematic of a parallel plate reactor

A parallel plate reactor is represented schematically in Figure 1.3. First operated in the early 1970's for semiconductor processing, parallel plate reactors are still the most commonly used source for industrial RIE applications. The system shown in Figure 1.3 consists, as the name suggests, of two parallel electrodes one of which is connected through a tuning box to an rf source. Typically the other electrode is grounded, although there are "push-pull" systems in which both electrodes are powered.

Generally the walls of the chamber are made of metal and so these can also act as a ground for the plasma. In effect this makes the area of the "grounded electrode" much larger than that of the powered electrode. This has an important effect on the behaviour of the plasma, in particular the potential distribution within the plasma, and hence on the ion energy

distribution (IED) at the surfaces. As discussed in Section 1.1 the IED is critical in determining etching rates and so it is important to understand the effect of unequal electrode areas.

1.2.2 *Inductive Sources*

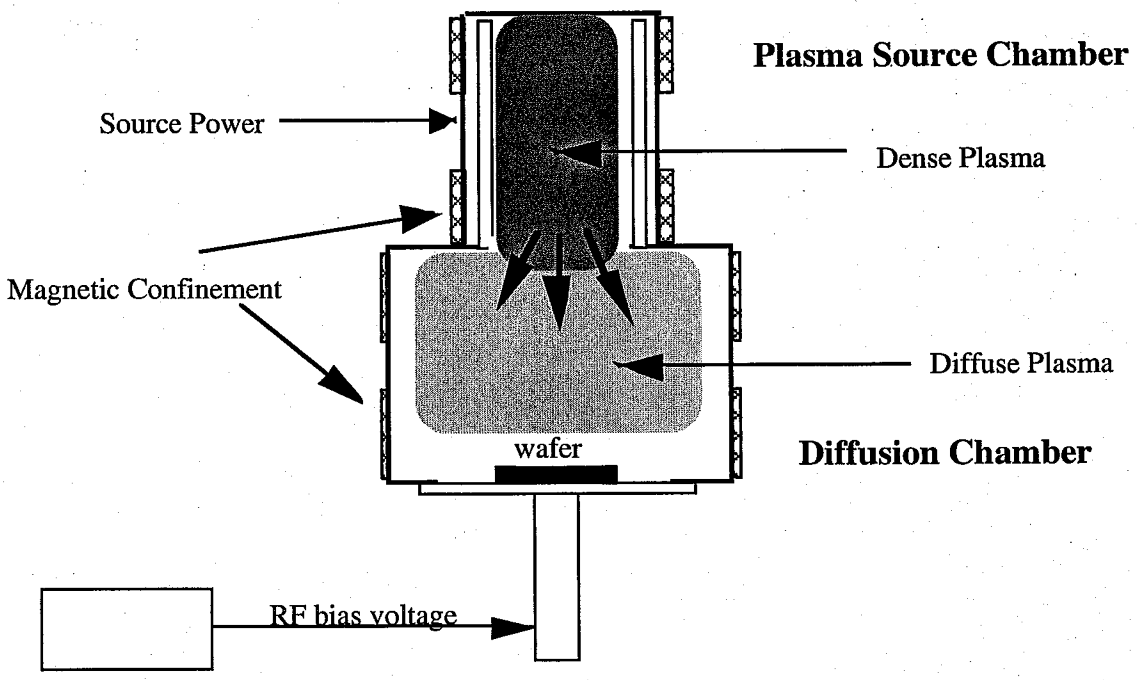

Figure 1.4 Schematic of an inductive reactor, showing source chamber where the plasma is produced and diffusion chamber in which the wafer is placed. Note that the wafer is biased using an rf voltage.

More recently, inductive sources have been used for processing applications. Generally they are more efficient at transferring energy to the electrons than rf sources, producing a high degree of ionisation and resulting in much higher plasma densities. This allows a new configuration in which the source tube (where the plasma is produced) is physically separated from the processing chamber where the wafer is placed, and the plasma diffuses from the source into the processing chamber. The wafer can be biased separately using an rf source. The processing chamber can also include magnetic confinement in order to improve plasma containment and maintain higher plasma densities. A diagram of this type of reactor is shown in Figure 1.4. The energy for the source plasma can be produced by microwave coupling, or by an rf source such as a helicon antenna (Boswell (1984)).

The high degree of ionisation in these sources and the resulting large plasma densities result in very efficient etching and deposition processes. Since these sources can be run at low pressures, the ion mean free path can be made much larger than the sheath width, to give anisotropic angular distributions at the wafer surface. Using separate power sources to produce the plasma and to bias the wafer allows separation of the ion bombardment energy and ion current. This is unlike parallel plate reactors in which the voltage applied to the wafer directly determines the plasma density. The separate biasing of the wafer therefore allows much better control of the IED at the wafer surface, particularly since plasma potentials for these reactors are relatively low: of the order of 10 – 20V. An rf bias voltage is generally used, since wafers are typically made of insulating materials and so must be capacitively coupled to the source, which precludes the use of dc biasing.

1.3 Plasma Modelling Techniques

Low pressure capacitively coupled rf systems have been intensively modelled over the past twenty years or so, because of their technical applications in the materials processing industry. A plasma can be fully described by a coupled solution of both the Boltzmann and Poisson's equation, but a general formulation can only be found numerically.

Boltzmann's equation, derived over 100 years ago, describes the continuity of f, the particle distribution function, in 6-dimensional space (3 dimensions each of position and velocity). For a single charged species, which can interact with j neutral species, the generalised Boltzmann equation is given by:

$$\frac{\partial \mathbf{f}}{\partial t} + \mathrm{v}.\nabla_r \mathbf{f} + \frac{e\mathrm{E}}{m}.\nabla_r \mathbf{f} = \sum \iint \left[\mathbf{f}(\mathbf{v}',\mathbf{r},t)\mathbf{F}_j(\mathbf{V}'_j,\mathbf{r},t) - \mathbf{f}(\mathbf{v},\mathbf{r},t)\mathbf{F}_j(\mathbf{V}_j,\mathbf{r},t)\right], \\ \times \mathrm{v}_{\mathrm{rj}}\, \sigma_j(\theta,\mathrm{v}_{\mathrm{rj}}) d\Omega_j d\mathbf{V}_j \tag{1.1}$$

where $\mathbf{v}_{\mathbf{rj}} = |\, \mathbf{v} - \mathbf{V}_{\mathbf{j}}|$

$d\Omega = \sin\theta d\theta\, d\phi,$

f, **v** are the distribution and velocity of the charged species, and $\mathbf{F}_j$, $\mathbf{V}_j$ are the distribution and velocity of the j^{th} neutral species. The left hand side of (1.1) describes the evolution of **f** due to collisionless motion in an externally applied electric field, and the right hand side describes the changes due to binary collisions with the j^{th} neutral species, where σ_j is the velocity dependent differential cross-section of the j^{th} neutral species, and θ is the angle of collision. Separate equations must be derived and applied to each charged species of interest in the plasma.

Poisson's equation is given by:

$$\nabla^2 \phi = -\frac{\rho(\mathbf{r},t)}{\varepsilon} \tag{1.2}$$

where ϕ is the potential, ρ is the charge density and ε is the plasma permittivity. Obviously finding a coupled solution for both of these equations is extremely complex, and in general the system is too difficult to solve for all species using all dimensions, even numerically.

In deciding what method to use in modelling their plasma, researchers must decide on what will best suit the intended goals. Analytic models, for instance, tend to take a much more simplistic view, with the intention of predicting some of the generalised basic behaviour of the plasma without going into detail. Often this is accomplished by extensive simplification of the physics, and can neglect some of the more interesting phenomena occurring in the plasma. Numerical modelling on the other hand can reproduce in some detail effects which are observed experimentally, and have even been used to predict phenomena which were later measured experimentally, for example stochastic heating of electrons in the sheath (Graves (1987), Vender and Boswell (1991) and Turner and Hopkins (1992)). However numerical results tend to be specific to the parameters specified in the model (e.g. pressure, frequency, voltage, gas type) and are not very useful for predicting generalised behaviour. Numerical modelling of rf plasmas typically follows one of two approaches – fluid or kinetic. The two methods are differentiated in the way they go about solving the Boltzmann equation.

One of the problems with modelling is that systems which are actually designed for processing applications, generally have complex geometric structures and produce plasmas with complicated chemistries, often with unknown compositions of charged and radical species. This makes it extremely difficult to model the systems, particularly since many models are restricted to one spatial dimension, and many of the reaction cross-sections are unknown. To facilitate development of models and to promote an understanding of the basic plasma physics, as distinct from the plasma chemistry, a number of experimental systems have been designed specifically for comparison to plasma models (Hargis *et al* (1994), Godyak *et al* (1990)). These use symmetric geometries and are generally run with non-reactive gases, such as helium and argon.

A brief (and by no means comprehensive) summary of analytic rf modelling is presented in Section 1.3.1. Some of the assumptions and drawbacks of these models are discussed. Section 1.3.2 looks at equivalent circuit models. Sections 1.3.3 discusses fluid methods, and Section 1.3.4 examines the kinetic approach. In section 1.3.5 a short history of Particle-in-cell (PIC) techniques is given, together with their application in studying low pressure rf plasmas. Finally Section 1.3.6 looks at the recent emergence of hybrid simulations to deal with restrictions inherent in both fluid and kinetic schemes.

1.3.1 Analytic Models

Analytic models of plasmas have a long history, going back some 100 years, and in that time many different methods have been used. Analytic models, by necessity, must include some quite sweeping assumptions and simplifications in order to make the equations tractable. Generally speaking analytic models are restricted to one spatial dimension, and often temporal and spatial averages of plasma parameters are used. Smirnov and Tsendin (1991), for example, average over the fast temporal and spatial variation of the electrons in a semi-analytic rf plasma model. Plasma species are limited, with most models considering only ions and electrons explicitly. Particle interactions are generally restricted to collisions with background neutrals (e.g., ionisation and elastic scattering for the electrons and charge exchange for the ions) and chemical effects are ignored altogether.

It can be difficult to classify analytic models as each uses different assumptions, depending on the simplifications intrinsic to the system to be modelled and the intentions of the modeller. The general intention of most analytic models is to determine simple expressions for the "internal" discharge parameters, such as the electron temperature, plasma density and current-voltage characteristics, as functions of the known applied parameters – voltage, frequency, electrode spacing and gas pressure.

Langmuir developed one of the first analytic models of a dc plasma. He used a simplified kinetic model, assuming a Maxwellian electron distribution and cold ions, together with Poisson's equation, to obtain an integrodifferential equation (known as the plasma-sheath equation). This was solved separately for the sheath (Langmuir and Blodgett (1921)) and bulk regions (Tonks and Langmuir (1929)). Another approach to the sheath problem was derived in the late 1940's by Bohm, in which a minimum value is specified for the ion energy distribution at the bulk-sheath interface, where the cutoff energy is determined by requiring a monotonically decreasing potential in the sheath (see references in Emmert *et al* (1980)). Although derived for dc conditions, versions of both methods can be used to determine ion transport in rf plasmas when the applied frequency is much larger than the ion plasma frequency. Under these conditions inertia limits the ion response to the average (or dc) fields. Numerical kinetic models (Emmert *et al* (1980), Bissell and Johnson (1987)) have been used to examine density and potential distributions and the ion flux in the pre-sheath; and an analytic version for both sheaths and bulk is presented in this thesis (Chapter 3).

In the early 70's Godyak (1976) derived a quite complete analytic model of a low pressure, planar, rf plasma. The model used an equivalent circuit to describe the plasma in terms of bulk and sheath impedances, together with particle and power balance equations. This model was extended to include an inhomogeneous ion density distribution in the sheath together with ion collisions (Godyak and Ganna (1980)). Godyak and his collaborators have also looked at power dissipation in the rf plasmas (Popov and Godyak (1984), Godyak, Piejak, and Alexandrovich (1991a)), and the model has been used in an extensive comparison to the experimentally determined electrical characteristics of an argon plasma (Godyak, Piejak, and Alexandrovich (1991b)). Misium *et al* (1989) have also determined a self-consistent macroscopic model of a planar rf discharge, including particle and energy balance equations, to determine the sheath dynamics, electron temperature, density and the electron power balance; finding qualitative agreement with experimental measurements in an argon plasma.

In many cases researchers have derived models which deal specifically with one region or one process occurring in the plasma. Sheath dynamics, in particular, are of importance in low pressure rf plasmas, since most of the interesting particle-field interactions occur in this region and the sheath is instrumental in determining the charged particle distributions. Lieberman (1988) determined an analytic solution for a collisionless rf sheath which is similar to the dc Child-Langmuir sheath law, but also takes into account the non-zero time-averaged electron density in the sheath. At the densities typical of rf plasmas, the applied frequency lies somewhere between the ion and electron plasma frequencies, so the massive ions respond only to the average fields in the sheath, while the electrons respond directly to the rf variation. Godyak and Sternberg (1990) have used a semi-analytic approach, and Wood *et al* (1991) a circuit model, to derive the non-linear sheath dynamics in this frequency domain. Both obtained good agreement with experiment. Strongly non-Maxwellian electron energy distributions are a feature of electron interaction with the sheath. This effect and the resultant heating of the electrons due to stochastic or sheath heating has been well studied (Popov and Godyak (1984), Goedde *et al* (1988), Okuno *et al* (1992), Godyak and Piejak (1993), Katsch *et al* (1993)). Electron heating is examined further in Chapter 4.

As discussed in Section 1.2 the ion impact energy at the substrate is an important parameter for processing applications, which necessitates knowledge of the behaviour of the ion distribution in the sheath. Bimodal energy distributions in collisionless ion plasmas have been well studied (Coburn and Kay (1972), Metze *et al* (1989), Field *et al* (1991), Hamaguchi *et al* (1992)); Wild and Koidl (1989) and (1991) derived a model for asymmetric rf discharges, including the effects of charge-exchange with neutrals. The ion energy distributions are found to have a complex structure of peaks, due to the coupling between collisions in the sheath and the rf fields. The theoretical results are found to have good comparison with experiment.

The Bohm criterion is often used in models to couple the ion dynamics between bulk and sheath solutions, however rf effects on this criterion have been largely unexplored. Meijer and Goedheer (1991) derive the Bohm criterion for rf plasmas, and find it is somewhat lower than the dc limit. Boswell *et al* (1992) derive a limit for an electronegative rf plasma, and find the criterion is linked to the negative ion temperature (and is therefore of the order of the ion temperature). They present qualitative agreement of the theoretical results with a PIC simulation.

Most of the models discussed above have been for symmetric systems, in general asymmetric systems have not been extensively studied. Lieberman has developed analytic models to determine the voltage division in spherical geometry (1989a), as have Song *et al* (1990), and the bias voltage in a two-dimensional cylindrical model (Lieberman and Savas (1989)). Raizer and Shneider (1992) present a model, also in spherical geometry, to determine the sheath dynamics and the time-dependent behaviour of the rf current.

1.3.2 Circuit Models

Plasmas have well-defined electrical characteristics, which can be reproduced using an equivalent circuit, in which plasma impedances are modelled as the appropriate electrical components (resistors, capacitors, inductors etc). This method is simple and straightforward, and experimentally measured values of the impedance can be used directly in the equations. This allows determination of, for instance, rf and dc sheath voltages, as a function of input parameters such as the source voltage, frequency, and pressure, without requiring a fundamental understanding of the plasma physics. At rf frequencies the sheath is found to be essentially capacitive, with low conduction currents and large electric fields, while the bulk region is essentially field-free. Generally speaking models have reflected this by separating the sheath and bulk circuits – a generalised model, from Godyak *et al* (1991b) is shown in Figure 4.19. The sheath impedances are mainly capacitive but include parallel resistive losses due to ion acceleration through the sheath. The bulk impedance is mainly resistive, due to electron-neutral collisions (and is therefore a function of the background gas pressure), but at high frequencies a parallel inductance must be included to take into account effects due to electron inertia. In the rf plasmas of interest to this thesis, the impedance is predominantly capacitive (i.e., the rf current lags the voltage by approximately 90°) and so the sheaths produce the dominant impedance characteristic of the plasma.

Logan, Keller and Simmons (1977) determined a model for an rf sputtering system, using a circuit model together with empirical fittings for the plasma density, sheath thicknesses and power. Keller and Pennebaker (1979) derive a model which includes ion flux to determine the rf and dc electrical parameters of the system from the input rf power and voltage at the target. This model was also used to characterise sputtering systems. Wood *et al* (1991) used an equivalent circuit to model a floating probe in an rf sheath, in order to relate the observed probe voltage to the non-linear sheath motion. Klick (1993) derived a 1-D resistive model for applied frequencies less than the ion plasma frequency (so that ions can respond to the instantaneous fields) which solves for the sheath potentials by expanding the sinusoidal sheath motion/voltage as a Fourier series. A dc ion current is included to model the effect of electrode asymmetry, and extra electrodes can be added to represent the effect of inserting probes on the plasma.

Circuit models have been extensively used to predict the effects of asymmetric electrode areas on the sheath voltages. Generally speaking the electrodes in processing reactors are not symmetric, particularly if the area of the walls is also taken into account (see Figure 1.3). Etching rates are dependent on ion energy, and hence on the average sheath voltage at the substrate. A number of models (Koenig and Maissel (1970), Coburn and Kay (1972), and Horowitz (1983)) have attempted, with varying degrees of sophistication, to determine the ratio of the average sheath voltages as a function of the area ratio of the electrodes.

1.3.3 Fluid models

Fluid theory, otherwise known as moment or continuum theory, involves the solution of one or more moments of the Boltzmann equation. The charged species in the plasma are modelled as a fluid using equations of particle continuity and energy conservation; particle density, momentum and energy can be determined from the moments of the Boltzmann equation and Poisson's equation is used to determine the potential distributions. However this system of equations is not closed and so generally an assumption of local equilibrium, in which the particle kinetics are assumed to be determined by the local electric field, is used to complete the specification of the system. Typically this is true for high pressure plasmas in which the mean free path for particle collisions is much smaller than the reactor length. This representation is therefore not very good at modelling non-equilibrium systems in which electron distributions are far from Maxwellian, as is typically true of low pressure rf discharges. Hence these codes are not really adequate for modelling the sheaths which have large, rapidly varying fields. Some researchers have circumvented this problem by introducing specific assumptions (discussed later in this section) or by using hybrid codes which combine fluid and kinetic techniques (see Section 1.3.6).

The moments of Boltzmann's equations give a set of coupled, time-dependent partial differential equations which must be solved in space and time. To make the problem more tractable, simplifying assumptions are introduced. Commonly these include representing the plasma by fewer than 3 spatial dimensions, and using total particle flux rather than particle momentum; often the electron energy distribution is not resolved. The coupling between moments of the Boltzmann equation and Poisson's equation is a difficult numerical problem, and as previously mentioned the assumption of local equilibrium has commonly been used as a closure condition. Some commonly used methods of solving the system of equations are described below, together with a brief description of their applications.

One of the first methods used is explicit finite difference solution of the equations on mathematical meshes in time and space. For rf applications the periodicity of the problem in time has been exploited by assuming harmonic steady-state solutions. Graves and Jensen (1986) used a series expansion of the equations to solve a two-moment fluid model, representing a parallel plate rf (13.56 MHz) argon-like discharge for a pressure range of 0.5 - 50 Torr. They found spatiotemporal results of the electron temperature, plasma density, and the potentials. Barnes *et al* (1988) use transport coefficients calculated using Monte Carlo techniques to determine plasma potentials, and bias voltages as a function of area ratio and rf power. They also discuss numerical instabilities associated with explicit techniques (see also Barnes *et al* (1989)) including numerical diffusion introduced in the presence of large moment gradients. Park and Ecconomou (1990) used a similar method to look at both argon and chlorine discharges, to determine the differences between electropositive and electronegative discharges.

One of the problems with using explicit finite difference methods is the stability restriction on the size of the time-step, which can make the codes relatively time-consuming to run. To allow the use of a longer time-step, and thus reduce run times, Boeuf (1987) introduced implicit methods of solving the fluid equations. A one-moment model was used to look at the effect of frequency and gas composition (electropositive or electronegative) on the plasma parameters, in particular examining the formation of double-layers at the sheath boundary in electronegative discharges. Belenguer and Boeuf (1990) modelled the transition from α (low power) to γ (high power) modes in a helium discharge. This corresponds to a change in the sustaining mechanism of the discharge, from high energy electrons produced by the moving sheath edge, to secondary electrons accelerated through the sheath. To model the non-Maxwellian distributions inherent in electron-sheath interactions, high and low (bulk) energy electrons were modelled as two separate groups. Oh *et al* (1990) also used implicit methods to study an electronegative discharge. Meyyappan and Govidaan (1991) have included convective and local acceleration terms to derive a three-moment model of rf discharges in argon and chlorine at a pressure of 300 mTorr.

As previously mentioned numerical diffusion occurs when moment equations are solved in regions of steep gradients. A popular (ad hoc) solution to this problem is to use flux corrected techniques (Kunhardt and Wu (1987), Tsai and Wu (1990), Sato and Tagashira (1991)).

Fluid models have also been used to look at problems in the sheath and pre-sheath. One-dimensional collisionless ion flux to a boundary is modelled in Bissell *et al* (1989) and for both collisional and collisionless regimes by Scheuer and Emmert (1990). Zawaideh *et al* (1990) examine the Bohm criterion for collisional to weakly collisionless ions. Ions are made collisionless by leaving out the explicit collisional terms in the code, although coulomb collisions, implicit in the formation of the fluid equations, remain.

1.3.4 Kinetic Models

Kinetic models (including PIC and convective schemes) fully resolve the particle distribution functions in space and time. This is done by integrating Boltzmann's equation, either statistically and using Monte Carlo techniques to model collisions, as in PIC, or directly as for convective methods. These methods, therefore, are ideal for studying non-equilibrium plasma conditions in which the particle distributions are not necessarily directly related to the local fields. They are also particularly useful for following individual particle trajectories, which is useful for determining ion energy and angular distributions at surfaces in the plasma. PIC simulations are discussed in detail in the next section, and so this section looks at Monte Carlo, convective and other kinetic models.

Monte Carlo (MC) models typically follow particle trajectories in imposed electric fields, and so the motion of the charged particles has no feed-back on the field distribution. However, despite the restrictions of not being self-consistent, they can provide useful information about the plasma. Kushner (1983) used an MC simulation of a parallel plate argon rf discharge to determine the plasma density and average electron energy as a function of position. May *et al* (1993) also simulated an argon discharge to determine the electron EDF for both primary and secondary electrons. A great many authors have looked at ion trajectories through the sheath to determine the ion distributions at the electrodes. In particular MC models have been used to study the effect of isotropically scattered collisions with neutrals in the sheath on energy and angular distributions (Kushner (1985), Thompson *et al* (1988), Manenschijin and Goedheer (1991)). Sommerer and Kushner (1991) look at the distribution of hot neutrals arriving at the electrode, due to charge exchange collisions in the sheath. Liu *et al* (1990) include a differential cross-section for argon, to determine the effect of anisotropic scattering on the energy/angular distributions. They compare results from their model to experimental measurements, and find reasonably good qualitative agreement.

The convective model was developed at University of Wisconsin by W.N. Hitchon and co-workers. This method uses an algorithm based on Green's functions to determine the transport equations, which allows a much larger time-step than possible for finite difference methods (Hitchon *et al* (1989)). The convective technique has been used in a number of applications, including examining the cathode fall in a helium dc discharge (Sommerer *et al* (1989a)) and determining electron heating and distribution functions (Sommerer *et al* (1989b), Sommerer *et al* (1991)) in an rf helium discharge. A reduction in the time taken for convergence is introduced by use of a "scaleup" procedure (Hitchon (1991)).

Emmert *et al* (1980) solved the plasma-sheath equation with a finite ion temperature in the presheath to determine an analytic solution for the bulk potential and the ion flux and energy entering the sheath. Paranjpe *et al* (1987) used a coupled electron and chemical kinetics model to determine self-consistent diffusion of etchant species to the wafer, and thus determine etch rate as a function of power, pressure and flow rate. Boiko *et al* (1989) solve the ion transport equations self-consistently with Poison's equation and include heating of the background gas, to study redistribution of neutrals in a chlorine discharge.

1.3.5 PIC Models

A comprehensive review of the history and development of particle-in-cell (PIC) simulations, together with a summary of the basic techniques is given by Ned Birdsall (1991), one of the pioneers of the use of PIC methods to model plasma processing technologies. PIC techniques were first used in the 1950s to investigate electrostatic effects such as plasma oscillations and the two-stream instability, with a method known as the electrostatic sheet model (Alder (1970), Chpt 1). The development of modern PIC techniques, as applied to low pressure processing plasmas, took place mainly in the

1970s and early 80s with the introduction of a particle shape factor (Langdon and Birdsall (1970)), inclusion of Monte Carlo particle collisions (Hockney and Eastwood (1981), Chpt 10), and finally using realistic boundary conditions (Birdsall and Langdon (1985)). Much of the theoretical work on effects of the spatial grid (Langdon and Birdsall (1970)), and analysis of time integration (Langdon (1979)) occurred at about the same time.

The techniques used in modelling bounded systems have been well described in a number of books and review articles (Hockney and Eastwood (1981), Birdsall and Langdon (1985), Tajima (1989), Lawson (1989), Vahedi *et al* (1993)). Recent modifications include the addition of an external circuit (Verboncoeur (1993)) for more accurate representation of processing systems, and the use of multiple time/space grid scaling (Friedman *et al* (1991)) to increase computational speed. The numerical methods used in the work for this thesis are discussed in Chapter 2, looking in detail at effects of modelling in asymmetric geometries which have not been included elsewhere.

PIC techniques are an increasingly important tool for understanding modern plasma physics, with applications in modelling both laboratory and space plasmas. PIC has been used to study rf discharges in both symmetric (Morey and Boswell (1988), Vender and Boswell (1990), Trombley *et al* (1991)) and asymmetric (Alves *et al* (1991), Kimke *et al* (1994)) geometries, ion transport in rf systems (Barnes *et al* (1991), beam-plasma effects (Boswell and Morey (1989)), plasma source ion implantation (or plasma immersion ion implantation), (Vahedi *et al* (1991), Wood (1993), Faehl *et al* (1994)), negative ions (Vender and Boswell (1991), Lichtenberg *et al* (1994)) and dusty plasmas (Boeuf (1992), Belenguer and Boeuf (1992), Choi and Kushner (1994)). Recently a PIC model was used to study the accuracy of common assumptions and approximations used in fluid models, by direct evaluation of the ion and electron momentum equations (Surrendra and Dalvie (1992)).

Like other kinetic models, PIC is particularly adept at modelling non-equilibrium plasmas, in which the particle distributions are not solely a function of the local fields. In particular they can reproduce extremely accurately experimental measurements of electron and ion energy distributions in both bulk and at the reactor surfaces (Vahedi *et al* (1993b), Surrendra and Graves (1990)). However in modelling a plasma with individual particles PIC codes suffer the drawback of being computationally intensive, and are also subject to numerical noise on the density and field distributions, which can pose limitations on running conditions to maintain numerical stability. The first problem has, and is still being, reduced by increasing computer speeds and quite complex one-dimensional simulations including several species and their interactions can be easily run on desktop workstations. Speed can also improved by using implicit techniques (Birdsall and Langdon (1985)), adjustable temporal and spatial grids (Friedman *et al* (1991)) and by vectorising code to run on parallel computer architectures (Liewer and Decyk (1989)). However, interactions between particles are very time-consuming as they are currently dealt with, and so far it has proved impractical to use PIC simulations in systems which contain many species and/or which are chemically complex. The second problem can also pose serious limitations on the conditions for which it is practical to run PIC simulations.

1.3.6 Hybrid Codes

Hybrid codes utilising two or more of the techniques discussed above are coming into increasingly common usage, as people try to solve more and more complex problems. By using a combination of fluid and kinetic techniques researchers can combine the advantages of both: computational speed while still accurately modelling non-equilibrium plasma conditions. The problem is, of course, numerically complex, and care must be taken to ensure that the two methods mesh compatibly. Particularly since these codes often employ other methods for reducing computational time, such as using different time scales for ions and electrons, or having a non-uniform spatial mesh. However, to self-consistently solve problems such as representing reactor geometry in two or three dimensions, modelling a larger range of plasma species and including complex chemical reactions between species, it is only possible to do this with hybrid techniques. Some hybrid codes and their applications are discussed below.

All modern PIC codes for modelling low pressure rf plasmas are actually hybrid PIC/Monte Carlo codes, but since they have already been discussed in the previous section no further comment will be made here. PIC/fluid schemes are also popular for modelling. Porteous and Graves (1991) have designed a two-dimensional cylindrical model of an inductive plasma, which includes magnetic confinement. Their technique uses fluid electrons and particle ions, since at high pressures with magnetic confinement the electron distribution is presumed to be essentially Maxwellian. Ion gyro-radii are of the order of the reactor geometry, and so ion trajectories are influenced mainly by the potentials in the system. This code has been used to model a typical ECR reactor which has a relatively narrow source region where power is deposited into the plasma (modelled analytically), opening out into a wider diffusion chamber (Porteous *et al* (1994)). Two-dimensional profiles of potential, electron temperature and ionisation rate have been generated, and the ion energy and angular distributions determined for an argon plasma. Li and Wu (1992) have derived an unusual PIC/fluid model which uses PIC methods to generate distribution functions, which are then evolved in time (including collisional effects) using moments of Boltzmann's equation. Results from three models, using from one to three moments of the Boltzmann equation, are presented in comparison to a standard PIC/MCC code, with good agreement between the three-moment model and the PIC code.

Hybrid fluid/Monte Carlo codes are also popular, in which a Monte Carlo scheme is used to find the electron distribution function; collision rates and transport coefficients calculated from the EEDF are then used in the fluid equations. Sommerer and Kushner (1992) use this method together with a model for neutral transport and chemistry to simulate in two dimensions the kinetics and reactions for a range of different gases and mixtures of gases in rf discharge plasmas (see also Kushner (1992)). Sato and Tagashira (1991) use a similar method to model a monosilane-hydrogen rf discharge in one dimension. They present results for the spatiotemporal variation of electric field and charged particle density, and examine the effect of the sticking coefficient on the profile of the radical distribution.

Other work which can be included in the hybrid category include a combined plasma surface model by von Keudell and Moller (1994), which models deposition of C:H layers for an ECR discharge in methane. Power deposition into the plasma is determined from experimentally measured values, and a homogeneous absorption profile is assumed; transport coefficients are also determined assuming a homogeneous plasma with a Maxwellian electron distribution. A coupled model detailing surface interactions is used to determine deposition rates, including re-etching, adsorption, desorption and reflection interactions, giving good agreement with experimental measurements.

1.4 Scope of this thesis

From section 1.2 most of the reactor geometries used for both industrial applications and for laboratory experiments are, in effect, not symmetric. As discussed in the previous section there are a number of models, both analytic and numerical, which look at the functional dependence of the plasma parameters on the externally applied variables in planar systems. However relatively few examine the effects of asymmetric geometry, and those that do have concentrated mainly on the division of voltage between the sheaths as a function of the relative electrode areas, or the magnitude of the self-bias voltage. A Particle-in-cell code in spherical coordinates was therefore derived to explore in detail the effect of asymmetric geometries on the macroscopic properties of the plasma, in particular to determine the effect of different degrees of asymmetry, but also to examine the effects of changing applied voltage, frequency and pressure in an asymmetric system. To the author's knowledge there have only been two other studies published on PIC modelling of rf discharges in asymmetric geometries, Alves *et al* (1988) which determined voltage ratios and bias voltage as functions of area ratio for spherical and cylindrical geometries, and Krimke *et al* (1994) which presented a case study of a cylindrical discharge in an axial magnetic field with a fixed area ratio.

An important aim of this thesis was to compare PIC results with existing analytic models, however when the time came it was found that there was a dearth of appropriate models to use (this is discussed in detail in the introduction to Chapter 3). Partially this is because in spherical geometry both sheath and bulk equations become non-linear, making them difficult to solve exactly. In this thesis both sheath and bulk equations have been solved using series method, and thus have approximate solutions which are not as neat as the corresponding planar equations. Nonetheless good agreement is found between the analytic model and the Particle-in-cell simulations, and some relatively simple equations have been derived to determine bulk properties, such as electron temperature and ion current in asymmetric systems.

Chapter 2

Particle-in-cell Techniques

The Particle-in-cell (PIC) technique is a well-established method of modelling plasmas, and has been used for approximately the last 15 years to simulate low pressure rf reactors. Several books (especially Birdsall and Langdon (1985) and Tajima (1989)) detail the methods used in PIC and describe the advantages and limitations of the technique, therefore this thesis will only present a brief outline of the methods used, concentrating on modifications required by the spherical geometry and the external circuit. Birdsall and the computational plasma physics group at University of California, Berkeley pioneered the use of PIC techniques for low-pressure, bounded plasma simulations and so the methods detailed in Birdsall's book are followed most closely.

The system modelled by the simulation consists of two concentric spherical electrodes, separated by 20cm gap in which the plasma is formed, and an external circuit. This is shown schematically in Figure 2.1. The inner electrode is connected to an rf source

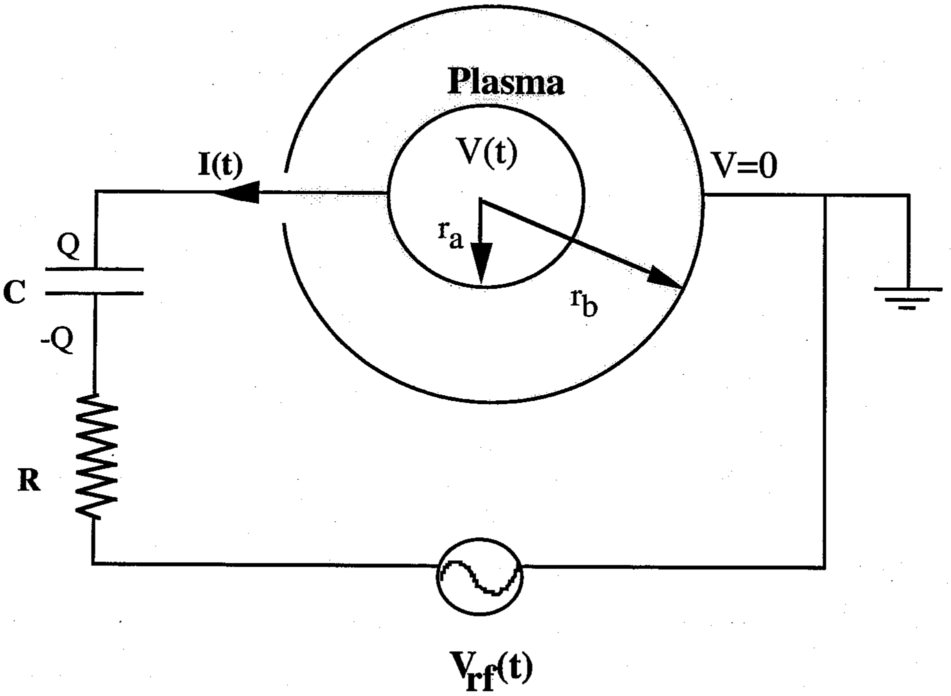

Figure 2.1 Schematic of plasma and external circuit, where r_a and r_b are the radii of the inner and outer electrodes respectively, *V(t)* is the voltage on the inner, powered electrode and $V_{rf}(t)$ is the rf source voltage.