1

Introduction

1.1 Plasmas

A plasma is an ionized gas containing freely and randomly moving electrons and ions. It is usually very nearly electrically neutral, i.e., the negatively charged particle density equals the positively charged particle density to within a fraction of a per cent. The freedom of the electric charges to move in response to electric fields couples the charged particles so that they respond collectively to external fields; at low frequencies a plasma acts as a conductor but at sufficiently high frequencies its response is more characteristic of a dielectric medium. When only weakly ionized (the most common situation for industrial applications) a plasma also contains neutral species such as atoms, molecules and free radicals. Most of this book is about weakly ionized plasmas that have been generated at low pressure using radio-frequency (RF) power sources.

Plasma is by far the most common condition of visible matter in the universe, both by mass and by volume. The stars are made of plasma and much of the space between the stars is occupied by plasma. There are big differences between these plasmas: the cores of stars are very hot and very dense whereas plasmas in the interstellar medium are cold and tenuous. Similar contrasts also apply to artificially produced plasmas on Earth: there are hot dense plasmas and colder less dense plasmas. In the former class are the fully ionized media encountered in research into controlled thermonuclear fusion for power generation, where the challenge is to confine a plasma that is hot enough and dense enough, for long enough so that light nuclei will fuse, liberating huge amounts of energy. The other class – the colder, weakly ionized plasmas also called low-temperature plasmas – includes those used in various industrial applications from lighting to semiconductor processing. Low-temperature plasmas are readily produced by electrical discharges through gases using sources ranging from DC to microwave frequencies (GHz). The gas pressure is typically between a fraction of one pascal and a few times atmospheric pressure (10^5 Pa).

When working in a DC mode and with emitting electrodes, atmospheric pressure discharges tend to operate in a high current regime. The current is carried in a narrow channel in which there is a plasma with its charged and neutral constituents in near-thermal equilibrium (all species comprising the medium having roughly the same temperature of about 10 000 K). Familiar examples can be seen in the giant sparks of lightning and in the arcs of electrical torches for welding and cutting. Arcs are not suitable for the treatment of soft surfaces because the neutral gas is too hot. However, severe gas heating can be avoided in atmospheric discharges if the conditions that allow thermal equilibrium are inhibited, leading to a general class of so-called 'non-thermal plasmas', in which electrons are markedly hotter than the ions and the gas atoms. One way to do this is with an RF-excited dielectric barrier discharge (DBD), in which electrodes are covered by a dielectric material so that charge build-up on the surface automatically extinguishes the discharge before the formation of an arc. These discharges operate with short repetitive pulses, often in a filamentary mode. Each filament carries a very weak current, but the local electron density and temperature are sufficient to dissociate and ionize a small but significant fraction of the gas. The neutral gas remains cold and the medium does not have time to reach thermal equilibrium during a current pulse. DBDs are growing in importance for low-cost industrial applications such as the sterilization of clinical materials and the removal of volatile organic compounds from air. In some circumstances some gases exhibit a more diffuse mode of DBD. A related class of discharge confines the plasma in a space that is too small for a thermal equilibrium to be established. At atmospheric pressure these are termed micro-discharges as the characteristic dimensions are sub-millimetre.

Low-temperature, non-thermal equilibrium plasmas are more easily generated on larger scales at lower pressure. The system is then composed of a vacuum chamber, typically several centimetres across, a throughput of feedstock gas and electrodes (or antennas) to inject electrical power. At low pressure, the discharge operates in the so-called glow regime, in which the plasma occupies the chamber volume as opposed to the filamentary modes generally observed at atmospheric pressure. Most of the volume is occupied by quasi-neutral plasma that is separated from the chamber walls and other surfaces by a narrow region of positive space charge. These boundary layers, or 'sheaths', typically extend over a distance of less than a centimetre. They form as a consequence of the difference between the mobility of electrons and positive ions. The potential structure in the plasma tends to confine electrons and to expel positive ions into the sheaths.

The absence of thermal equilibrium in low-pressure plasmas is important for their commercial applications since the electrical energy is preferentially transferred to electrons that are heated to tens of thousands of kelvin, while heavy particles remain nearly at room temperature. A distribution of electrons that has a temperature of 10 000 K contains a significant fraction that have enough energy to dissociate molecules of the feedstock gas into reactive species (atoms, free radicals and ions). The plasma thus converts electrical energy into chemical and internal energy that can be directed, for instance, into surface modification. Sheaths are also of major importance since they in turn locally convert electric field energy derived from the power supply into the directed kinetic energy of ions reaching the surfaces. Electric fields in the sheaths tend to accelerate ions perpendicular to the surfaces. The energy of ions bombarding any particular surface is a major parameter of process control that can readily be raised to thousands of times the energy that binds atoms together in small molecules and extended solids. These non-thermal phenomena account for the rich variety of plasma processing technology, from the surface activation of polymers to the implantation of ions in semiconductors.

Plasma processing technology is used in many manufacturing industries, especially in the surface treatment of components for the automotive, aerospace and biomedical sectors. Plasma technologies offer advantages in terms of environmental impact, through reduced use of toxic liquids, and in terms of engineering scale, through their compatibility with nanoscale fabrication. The biggest impact has certainly been in microelectronics, for which very large-scale integrated (VLSI) circuits could not be fabricated without plasma-based technologies. In the following sections some industrial applications of low-pressure radio frequency-plasmas will be described, setting the context for the more detailed analyses of later chapters.

1.2 Plasma processing for microelectronics

Integrated circuits (ICs) consist of several layers of carefully engineered thin films of semiconductors, dielectrics and conductors, fashioned *in situ* and interconnected by a very complex architecture of conducting tracks (see Figure 1.1). The thin films are deposited by means of plasma processes and are etched by reactive plasmas in order to form patterns of the order of a few tens of nanometres, i.e., a hundred times smaller than a human hair.

The basic element in the design of a large-scale integrated circuit is the metal-oxide-semiconductor field effect transistor (MOSFET) – see Figure 1.2. Most commonly the transistor is made in a layer of high-quality silicon grown onto a substrate of single-crystal, silicon semiconductor. The device regulates the flow of current from a ‘source’ region to a ‘drain’ region via a channel that is controlled by a gate electrode. The gate electrode is isolated from the channel by means of a few nanometres of dielectric, usually silicon dioxide. The MOSFET can operate as a very efficient switch for current flowing between the source and drain. The

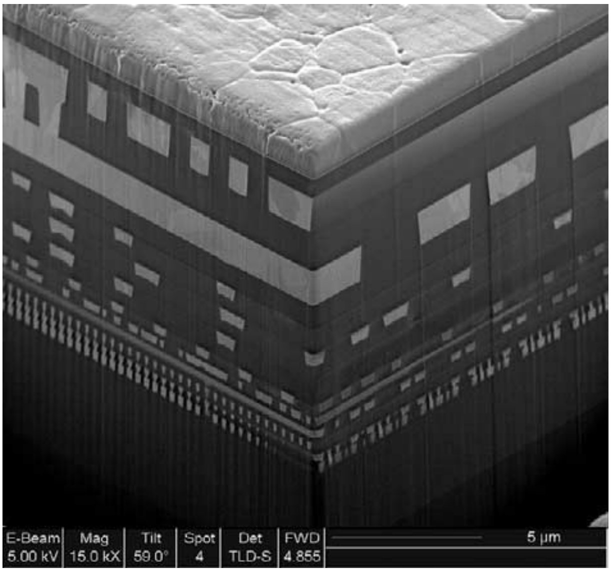

Figure 1.1 Multilevel metal dielectric interconnects in VLSI circuits.

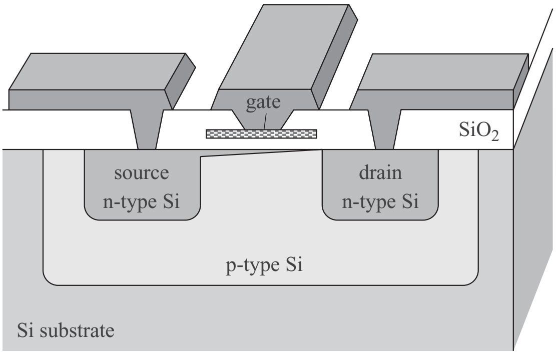

Figure 1.2 The structure of a silicon IC in the region of a MOSFET in which a gate electrode controls the formation of a channel of n-type silicon between source and drain regions.

switch is activated by biasing the gate. The gate size is the critical dimension in determining the level of integration and the speed of the device. In the technology known as CMOS (complementary metal-oxide semiconductor), the building blocks of memory and logic circuitry are based on devices that incorporate a MOSFET that has an n-type channel with one that has a p-type channel. CMOS technology is a dominant semiconductor technology for microprocessors, memories and application-specific integrated circuits. The main advantage of CMOS is its relatively low power dissipation.

A common description of the evolution of microelectronics technology is based on what is known as Moore's law. The prediction made by Gordon Moore in 1965 was that the number of transistors on the most complex integrated circuit chip would roughly double every two years. It has proved to be a remarkably good guide to the development of the IC market – a development that has been enabled by plasma-based processes.

1.2.1 Plasma etching

The principles of plasma etching are the following. In a first step, the substrate that bears the material which is to be etched is covered by a thin (<1 μm) layer of 'photoresist'. The photoresist is then patterned by exposure to UV through a contact mask, which creates a high contrast in the solubility of photoresist between areas that are exposed and areas that are shaded. The shadow pattern of the mask is next developed into the photoresist by means of wet chemistry to obtain open areas in the resist layer. The patterned wafer is then transferred to a plasma reactor. In the case of silicon-based materials the process gas is usually composed of one or more types of halogen-containing molecules (e.g. CF_4, SF_6, Cl_2 or HBr). The gas is introduced into the reactor where, on the formation of a plasma, it is dissociated by electron impact to form reactive species. In the case of SF_6, for instance, there are reactions with electrons (e^-) such as

$$\begin{aligned}
&e^- + SF_6 \rightarrow SF_5 + F + e^-,\\
&e^- + SF_6 \rightarrow SF_4 + 2F + e^-,\\
&e^- + SF_6 \rightarrow SF_2 + F_2 + 2F + e^-,\\
&\text{etc.}
\end{aligned}$$

The F atoms in the gas phase (g) are an effective silicon etchant, reacting with a surface (solid phase, s) to form a volatile etch product that may be pumped away:

$$4F(g) + Si(s) \rightarrow SiF_4(g).$$

In the absence of bombarding ions and crystallographic effects, the etching will proceed equally in all directions, i.e., isotropically, since the etchant atoms arrive without any specific directional influence, as shown in Figure 1.3(a). Isotropic profiles are also obtained in wet etching and are not suitable for the high aspect ratio etching required for dense integration (the aspect ratio is the ratio of the width of a feature to its depth).

In 1979, using a combination of atom and ion beams, Coburn and Winters [1] demonstrated that energetic ions arriving at a surface increase the effectiveness of etching with neutral atoms by more than an order of magnitude. This synergy is easily exploited in plasma reactors because plasmas naturally provide active

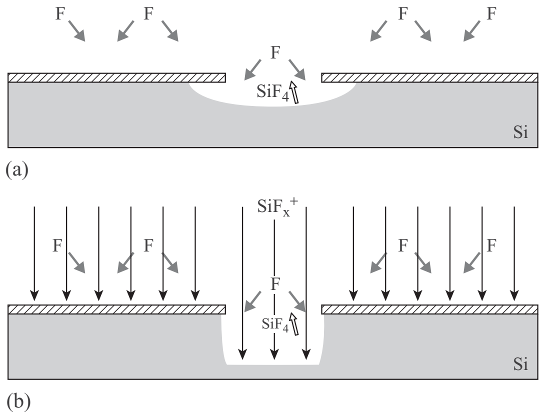

Figure 1.3 (a) Isotropic chemical etching; (b) anisotropic reactive ion etching.

neutral radicals as well as energetic ions that have been accelerated in the sheaths. Furthermore, owing to the sheaths, the ions have trajectories perpendicular to the surface, and they are found to increase considerably the etch rate perpendicular to the surface but to have little influence on the side-wall etching. Therefore, etching in the presence of ion bombardment tends to be anisotropic. The deliberate use of energetic ions to enhance the rate of etch reactions is known as reactive ion etching.

Q Suggest two factors that would link increased plasma density to higher (anisotropic) etch rates.

A The increased electron density will tend to increase the supply of radicals and therefore is likely to lead to a higher etch rate; the increased flux of ions to the surface will also tend to enhance the anisotropic etching.

Although ions can usefully introduce anisotropy to the etching, it is usually not sufficient to achieve the very high level of profile control required in CMOS technology. Polymerizing chemistries have therefore been introduced to add an etch-inhibiting coating to certain surfaces. When CF_4 is used as the feedstock gas the free radicals formed in the plasma, for instance CF and CF_2, tend to contribute to the growth of a polymeric film on the side walls of a feature, providing a so-called passivation layer. This layer does not form on the plasma-facing areas because it is continuously disrupted by the arrival of energetic ions, from a perpendicular direction. Fluorocarbon gases like CHF_3, CF_4, C_2F_6, C_4F_8 are known to be polymerizing and are routinely used to etch dielectric materials in microelectronics. In order to control the degree of polymerization, oxygen is often added to the gas to promote the formation of CO_2 on the surface, thereby competing with film growth. Polymerization is also a very efficient way to control the selectivity of a process, i.e., the ability to etch a specific material without affecting the underlying layer made of another material. A classic example is the capability of CF_4/O_2 plasmas to change the relative etch rates of Si and SiO_2 and hence the selectivity. An oxygen-rich mixture will etch pure Si faster than SiO_2 while an oxygen-lean mixture will etch SiO_2 faster than pure Si. Fluorocarbon plasmas have received a great deal of attention because a large number of the process steps in the manufacture of silicon ICs involve the differential etching of silicon and silicon dioxide [2–4].

Other halogen-based etching schemes are also important: one of the critical steps in CMOS is the etching of the gate stack, which is usually achieved in $Cl_2/HBr/O_2$ plasmas. Passivation this time involves the formation of silicon-based films of SiO_xCl_y [5]. Unwelcome process drifts have been linked to the deposition of these passivation layers on the reactor walls [6].

Plasma etching is also a key enabling technology in optoelectronics and photonics. For instance, the high aspect ratio, deep ridge InP-based heterostructure that is a vital building block in photonic device fabrication is readily manufactured by plasma processing. For this purpose, an etching process is required that can produce narrow, single-mode, ridge waveguides with smooth side-walls, free from undercuts or notches to minimize the optical scattering losses [7].

For removing large quantities of material in so-called ‘deep etching’ (on the order of tens of micrometres deep), plasma etching is again useful [8]. This is used in the fabrication of micro-electro-mechanical systems (MEMS), based on miniature gears, pivots, linkages, cantilevers, fluid channels and other components etched into silicon substrates; for harsh environments silicon carbide is preferred. Deep etching of these materials calls for high-density plasma sources to keep processing times within bounds. An example of the deep etching of silicon carbide is shown in Figure 1.4, where a helicon plasma was used (see Section 1.4) to form a dense plasma in a mixture of SF_6 and O_2 [9–11].

1.2.2 Plasma deposition

Plasma-enhanced chemical vapour deposition (PECVD) allows the deposition of a variety of thin films at lower temperatures than those utilized in classical CVD reactors. For example, whereas ordinary CVD of high-quality silicon dioxide films requires temperatures in the range of 650–850°C, similar quality films can be deposited at 300–350°C via a plasma-enhanced process. Again, the advantage of using plasmas comes from the fact that they are able to fragment molecules into reactive radicals, even at room temperature. For deposition, radicals that condense on the substrate are required to contribute to film growth (in contrast to etching where the chemistry is chosen so that radicals react with the surface to form volatile products).

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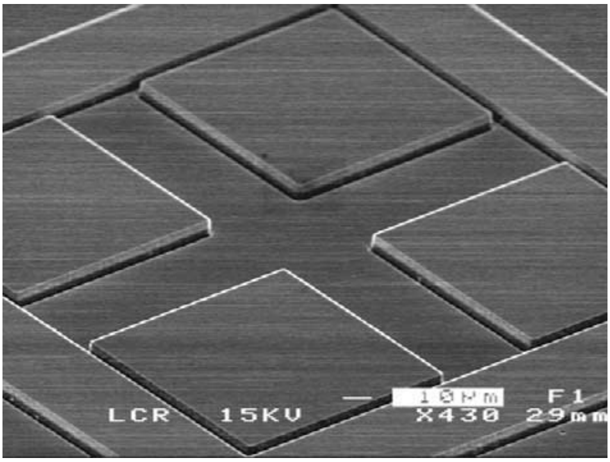

Figure 1.4 Deep micrometre-scale structure etched in SiC using a SF_6/O_2 helicon plasma.

Apart from microelectronics, one of the most important applications of PECVD is the fabrication of flat-panel displays [12]. Liquid crystal displays (LCDs) in particular have emerged as favourites for laptops and flat-panel monitors. When combined with a transistor switch at each pixel, the so-called active matrix display (AMLCD) readily achieves high resolution (several million pixels), large size, full colour and TV-compatible response times. An AMLCD is made of two glass sheets between which is a thin layer of liquid crystal. On one glass sheet is an array of thin film transistors (TFTs). Each TFT switches the voltage on a small indium tin oxide (ITO) transparent electrode that defines a pixel. The other sheet is covered by colour filters and a common electrode. The TFT array is manufactured by a series of plasma-based process steps that alternate thin-film deposition with patterning. A major challenge for the design of plasma systems that will form the TFTs is to do with maintaining control of the uniformity of the plasma over the entire area of the display – the larger the better so far as the market is concerned. Related issues of scalability will be discussed in more detail in later chapters.

Plasmas are also used in the physical deposition process known as sputtering that is commonly used for depositing metal layers on semiconductor circuits. In sputter deposition systems a low-pressure plasma provides ions (typically Ar^+) that are accelerated onto a metallic target that is negatively biased. The ions are given a kilovolt or so of energy by the acceleration so that when they collide with the target, atoms of the target are dislodged, or ‘sputtered’, forming a plume of ejected material. Sputtering is a purely physical, unpatterned, etching process. A substrate placed near a sputtering target is effectively sprayed with atoms from the

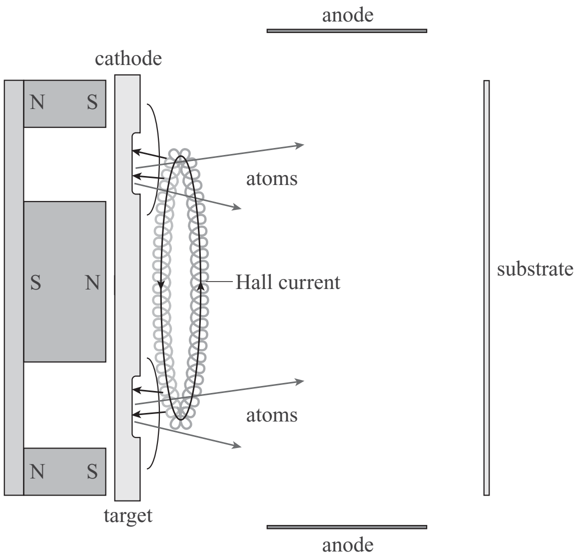

Figure 1.5 Schematic of a DC magnetron. Target material is sputtered most intensely from adjacent plasma created by the spiralling ring of electrons whose drift around the ring constitutes the Hall current.

target, building up a few tens of nanometres in a matter of minutes. A common configuration for sputtering uses a so-called magnetron arrangement, where a magnetic field is arranged parallel to the target surface so that electrons spiral round the field creating a locally intensified and efficient ionization of the gas. This is illustrated in Figure 1.5. A high-density plasma forms in a ring adjacent to the target, which is in turn more aggressively eroded in this region than elsewhere, owing to the intense ion bombardment. The forces on the electrons from the combination of the magnetic field and the electric field in the plasma push the spiralling electrons around the ring of intensified plasma, driving what is known as a ‘Hall current’. The geometry of electric and magnetic fields also occurs in one of the plasma thrusters discussed in the next section, for which the Hall current is a key feature.

1.3 Plasma propulsion

A rocket-propelled spacecraft in free flight receives its acceleration from expelling mass (the propellant). Its equation of motion is derived from a force equation that balances the rates of change of momentum of the spacecraft and the ejected matter:

$$m\dot{v} = -\dot{m}v_{\mathrm{g}}, \tag{1.1}$$

where m is the total mass of the spacecraft (including unspent fuel) at a given time, $\dot{v}$ is the magnitude of its acceleration, v_g is the magnitude of the exhaust velocity of the propellant (relative to the spacecraft) and $\dot{m}$ is the rate of change of the spacecraft's total mass due to mass expulsion ($\dot{m} < 0$). The challenge for space propulsion is to achieve the highest possible exhaust velocities and to fully ionize the propellant in order to make best use of it. This can clearly be seen after integration of (1.1) between any initial mass m_0 and some final mass m_f, for constant exhaust speed, which gives

$$\Delta v = v_g \ln \frac{m_0}{m_f}, \tag{1.2}$$

showing that for a given reduction in mass, the change in the spacecraft speed during a given period of acceleration is proportional to v_g. The propulsion community usually uses two quantities to characterize a thruster: the thrust $T = \dot{m} v_g$ and the specific impulse $I_s = v_g/g$, where g is the acceleration due to the Earth's gravity at sea level.

1.3.1 Conventional plasma thrusters

Electric propulsion techniques [13] may be separated into three categories: (i) electrothermal propulsion, in which the propellant is electrically heated and then expanded thermodynamically through a nozzle; (ii) electrostatic propulsion, in which ionized propellant particles are accelerated by an electric field; (iii) electromagnetic propulsion, in which current driven through a propellant plasma interacts with an internal or external magnetic field to provide a stream-wide body force. Here is a short description of the most common systems.

Resistojets and arcjets

These belong to the first category. In a resistojet the gas is heated via the chamber wall or a heater coil whereas in an arcjet the gas is heated by an electric arc. The propellant gas is then accelerated downstream through a nozzle. These thrusters have limited specific impulse (less than 1000 s) and face technological challenges owing to the high temperatures required.

Electrostatic ion thrusters

Positive ions are created in a plasma (DC, RF or microwave, usually magnetized) and accelerated out through a DC-biased grid. In order to maintain an overall charge balance, the ion beam must be neutralized downstream, via a thermionic filament or some other source of electrons. Electrostatic thrusters have been successfully demonstrated and they can provide very high specific