Chapter - 2
Processing Techniques for Silicon Thin Film Technology

For the growth of crystalline silicon thin films of different form (nc-Si/a-SiC, nc-Si/SiO$_x$, superlattice etc.), various deposition techniques were used at low temperature (<400 °C) among which physical vapor deposition (PVD) and chemical vapor deposition (CVD) process are of immense interest for their successful application in the low cost production of the photovoltaic and optoelectronic devices.

2.1 Physical Vapor Deposition (PVD)

In physical vapor deposition (PVD) processes, elementary silicon is being used for the growth which is dominantly depends on the ions that impinge on the substrate surface. Molecular beam epitaxy (MBE), pulsed laser deposition (PLD), sputter deposition and ion-beam deposition (IBD) are the most important PVD processes. MBE is the most commonly used one. In the process of MBE, to ensure a high mean free path of the particles and to avoid contaminations from the gas phase, the ultra high vacuum (UHV) conditions must be employed. A wide range of materials systems are grown epitaxially by MBE, e.g GaAs, Si, Ge etc for electronics. In pulsed laser deposition (PLD) of silicon thin film, a high power pulse laser beam is focused inside a vacuum chamber to strike a silicon target. This material, vaporized from the target (in a plasma plume), is being deposited on the substrate as a thin film. This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing silicon oxides films. Ion-beam deposition (IBD) uses only Si-ions for film growth. Special ion beam sources allow for a precise control of the ion mass and energy. However, only low deposition rates of the order of 1Å/s are obtained by IBD due to the low effectively of the sources. In addition to that, the most important unit for the physical vapor deposition process is the rf-magnetron sputtering which is discussed in section 2.1.1.

2.1.1 rf-Magnetron Sputtering

Sputter deposition is a physical vapor deposition process for depositing thin films where the sputtering means ejecting material from a target and depositing it on a substrate such as a silicon wafer (source material). Sputtering is extensively used in the semiconductor industry to deposit thin films of various materials in integrated circuits.
processing and many other applications. Thin anti reflection coatings on glass, which are useful for optical applications are also deposited by sputtering. Because of the low substrate temperatures used, sputtering is an ideal method to deposit contact metals for thin-film transistors also in addition to its utilization in fabrication of thin film sensors, photovoltaic thin films (solar cells), metal cantilevers and interconnects etc.

The basic process is as follows. A target, or source of the material desired to be deposited, is bombarded with energetic ions, typically inert gas ions such as Argon (Ar\(^+\)). The forceful collision of these ions onto the target ejects target atoms into the space. These ejected atoms then travel some distance until they reach the substrate and start to condense into a film. As more and more atoms coalesce on the substrate, they begin to bind to each other at the molecular level, forming a tightly bound atomic layer. One or more layers of such atoms can be created at will depending on the sputtering time, allowing for production of precise layered thin-film structures.\(^3\) See Fig 2.1.

![Fig. 2.1 Sputtering at the Molecular Level.](image-url)

Though the basic idea of operation is seemingly simple, the actual mechanisms at play are quite complex. Electrically neutral Argon atoms are introduced into a vacuum chamber at a pressure of 1 to 10 mTorr. A DC voltage is placed between the target and substrate which ionizes Argon atoms and creates plasma, hot gas-like phase consisting of ions and electrons, in the chamber. This plasma is also known as a glow discharge due to the light emitted. These Argon ions are now charged and are accelerated to the anode target. Their collision with the target ejects target atoms, which travel to the substrate and eventually settle. Electrons released during Argon
ionization are accelerated to the anode substrate, subsequently colliding with additional Argon atoms, creating more ions and free electrons in the process, continuing the cycle.

There are a number of ways to enhance this process. One common way to do this is to use what is known as a magnetron sputtering system. The main difference between this and a basic DC sputtering system described above is the addition of a strong magnetic field near the target area. This field causes traveling electrons to spiral along magnetic flux lines near the target instead of being attracted toward the substrate. The advantage of this is that the plasma is confined to an area near the target, without causing damages to the thin film being formed. Also, electrons travel for a longer distance, increasing the probability of further ionizing Argon atoms. This tends to generate stable plasma with high density of ions. More ions mean more ejected atoms from the target, therefore, increasing the efficiency of the sputtering process. The faster ejection rate, and hence deposition rate, minimizes impurities to form in the thin-film, and the increased distance between the plasma and substrate minimizes damage caused by stray electrons and Argon ions.

Depending on the target material either RF or DC sputtering may be used. If the target material is a conductor, a constant voltage can be used to accelerate the ions to the desired bombarding velocity. As the ions strike the surface, the resulting charges can move freely about the material to prevent any charge buildup. However, in case of insulator target, as the ions strike the surface, their charge will remain localized and over time the charge will build up, making it impossible to further bombard the surface. In order to prevent this, alternating current is used at a frequency above 50 KHz. At high frequency, the heavy ions cannot follow the fast switching of the applied electric field and accordingly, only electrons hit the surface to neutralize charge. Often an additional gas such as nitrogen or acetylene is used, which will react with the ejected material (reactive sputtering).

The Hind Hivac rf/DC magnetron sputtering unit, schematically shown in Fig. 2.2, is equipped with three 3-inch diameter planar magnetron cathode to facilitate the growth of thin films with pre-sputtering shutter and a rotatable substrate holder. The substrate can be heated up to 500°C to improve the film adhesion to the substrate. The ultimate pressure one can get in the sputtering chamber of this system is $7 \times 10^{-7}$ mTorr by a diffusion pump. The deposition can also be done in a reactive environment also by
introducing H$_2$, CO$_2$ etc. along the sputtering gas of Ar. In addition to that, the grid and substrate biasing can also be performed at the present sputtering unit described above.

![Illustration of the rf/DC-magnetron sputtering unit.](image)

**2.1.2 Thermal Evaporation**

One of the common methods of physical vapor deposition (PVD) is thermal evaporation. This is a form of thin film deposition, which is a vacuum technology for applying coatings of pure materials to the surface of various objects. The coatings, also called films, are usually in the thickness range of angstroms to microns and can be a single material, or can be multiple materials in a layered structure. The materials to be applied can be pure atomic elements including both metals and non-metals, or can be molecules such as oxides and nitrides. The object to be coated is referred to as the substrate, and can be any of a wide variety of things such as: semiconductor wafers, solar cells, optical components, or many other possibilities.$^{4,5}$

Thermal Evaporation involves heating a solid material inside a high vacuum chamber, taking it to a temperature which produces some vapor pressure (Fig. 2.3). Inside the vacuum, even a relatively low vapor pressure is sufficient to raise a vapor cloud inside the chamber. This evaporated material now constitutes a vapor stream,
which traverses the chamber and hits the substrate, sticking to it as a coating or film. Specification of the system includes tungsten or Molybdenum filaments to heat evaporants. The ultimate chamber pressure can be achieved up to $2 \times 10^{-6}$ mTorr. The typical filament currents are 10-20A.

The major advantages of the thermal evaporation unit over rf-magnetron sputtering unit are as – (a) it is simple and cheap, (b) less substrate surface damage and (c) excellent purity of films. However certain disadvantage makes the thermal evaporation technique unsuitable for silicon thin film deposition except deposition of metal for particular device application, e.g. metal electrodes etc. The disadvantages are as follows – (a) limited to low melting point metals, (b) it is not possible to evaporate the dielectric materials, (c) filament limits the amount of material that can be deposited and (d) density and adhesion are poor.

### 2.2 Chemical Vapor Deposition (CVD)

Typically, in the chemical vapor deposition process, the source gases is decomposed by means of providing thermal energy which requires substantial heat generation in the deposition chamber. However, to decompose the source gases at low temperatures, a wide variety of excitation methods are in use, e.g. plasma enhanced CVD (PECVD), hot wire CVD (HWCVD), and electron cyclotron resonance CVD (ECR-CVD). Growth
processes in CVD include the formation of precursors, consisting of Si-radicals in the case of SiH\textsubscript{4} as source material. Subsequently, these precursors are being physically deposited on the substrate, followed by the chemically absorptions of the silicon atom and the evaporation of the remaining hydrogen atoms. Being deposited on the substrate, the precursors experiences the surface reactions which are principal parameter in governing the nature of the silicon thin films. However, these surface reactions could not significantly in which the plasma generate a high amount of Si-radicals that may be directly physically absorbed. This surface reaction is thermally activated by the substrate temperature, and consequently, the deposition rate of CVD reactions is limited by the substrate temperature.\textsuperscript{6}

### 2.2.1 The RF-PECVD Process

Plasma enhanced chemical vapor deposition (PECVD) has become an established commercial technique for the deposition of a number of important materials, especially insulating films such as silicon oxide, silicon nitride, silicon carbide, micro/nano-crystalline silicon etc.\textsuperscript{7-12} The major advantage of PEVCD is its lower temperature capability compared to that of thermally driven CVD. For example, deposition temperatures of 700\degree C to 900\degree C are required to deposit silicon nitride, silicon carbide or silicon oxide films by thermal CVD, whereas only 250\degree C to 350\degree C is sufficient to deposit similar films by PECVD.\textsuperscript{13} This lower temperature capability is made possible by the addition of electrical energy to the CVD environment, and the effective substitution of this electrical energy for thermal energy. Applications of PECVD thin films and coatings range from electronics to optics and metallurgy. PECVD is also investigated for the deposition of crystalline films for microelectronics, such as polycrystalline silicon, microcrystalline silicon (\textmu c-Si), nanocrystalline silicon (nc-Si).\textsuperscript{14, 15}

Decomposition of a gaseous silicon source, such as SiH\textsubscript{4}, is the basic principle of all CVD-processes. In the simplest case, this decomposition is achieved by the thermal energy of the substrate. This thermal CVD is used in semiconductor industry and results in high quality silicon films with acceptable high deposition rates. However, at low temperatures, a wide variety of excitation methods for the decomposition of the gases have been utilized. Different kinds of PECVD techniques that are used for deposition of Si based thin films are radio-frequency capacitively coupled PECVD, inductively coupled PECVD, direct current (DC) PECVD, and very high frequency
VHF-PECVD, electron cyclotron resonance CVD (ECR-CVD). Among them, the 13.56 MHz (RF PECVD) is widely used in industrial scale. This technique takes advantage of a high energy electrons present in glow discharges to dissociate and ionize gaseous molecules, thereby forming chemically active radicals and ions. Since thermal energy is not needed to break chemical bonds, a variety of materials can be deposited on temperature-sensitive substrates (e.g. polymers or low melting point metals). The plasma environment in PECVD performs two basic advantages over thermal CVD. First, reactive chemical species are generated by electron impact collisions, thereby overcoming kinetic limitations that may exist in CVD processes. Second, the discharge supplies energetic radiation, primarily positive ions, but also neutral and metastable species, electrons, and photons, which bombard surfaces immersed in the plasma and thereby alter surface chemistry. Specifically, ion bombardment of growing film surfaces plays a key role in nucleation, growth kinetics, film composition, structure, and stress.

### 2.2.2 Capacitively coupled plasma enhanced CVD Technique

All thin films deposited in the present work for the Chapter 4 were carried out in a four chamber PECVD reactor, schematically represented in Fig. 2.4. The capacitively-coupled radio-frequency (RF) glow discharge is confined in a cylindrical stainless steel plasma chamber between two parallel plates’ circular electrodes of 6 inch in diameter and separated by a distance of 1.6 cm. The sample-holder is equipped with a thermocoax resistance which allows rising the temperature of the sample up to 200 °C. The pumping is achieved by two independent systems. The first one, composed of a rotary and a turbo-molecular pumps, produces a high vacuum of $1 \times 10^{-6}$ Torr before the deposition. The second system, used to pump the reactive gases, consists of a rotary vane and a Booster pump. Various pressure gauges like Perini gauge, penning gauge, and absolute gauge are used to measure the vacuum pressure and pressure during the deposition. Power is being feed to the plasma chamber by a 13.56 MHz rf-generator which is capacitively coupled through two parallel-plate circular electrodes producing a high density and low temperature plasma. Flow rates of different gases are controlled by Mass-Flow-Controller (MKS). In this system, there is also the provision of using different diluents gases like Helium, Hydrogen, and Argon.
Although capacitively coupled plasma (CCP) systems have been of versatile use in thin film industries for a long time, many high density plasma systems e.g., microwave electron cyclotron resonance (MW-ECR), helicon wave and inductively coupled RF plasma chemical vapor deposition (ICPCVD), etc., play a significant role in recent years, particularly in the development of the nano-crystalline silicon network. Among those, ICP has been attracting increasing attention due to its unique remote plasma characteristics which reduce ion bombardment effects. In comparison with the conventional capacitively coupled plasma sources, the ICPs operating in the electromagnetic mode have several major advantages e.g., they possess: (i) high densities of the plasma species, in particular, the electron number density $N_0 \approx 10^{12} \text{ cm}^{-3}$ at 10 mTorr, (ii) low plasma sheath potentials (several or tens of volts) near the chamber wall or deposition substrate, which is beneficial for the reduction in ion bombardment on the deposited films, (iii) low electron temperatures (a few electron volts) under a broad range of discharge conditions, and (iv) excellent uniformity of the plasma parameters in the radial and axial directions.$^{16,17}$

The nanocrystalline silicon in amorphous silicon carbide films (nc-Si/a-SiC) have been prepared by a planner inductively coupled plasma (ICP) CVD system excited
by radio frequency (rf) of 13.56 MHz. A schematic representation of the deposition system is shown in Fig. 2.5. The plasma is created within cubic stainless steel chamber with each side 30 cm. The inflow rate and pressure of the working gas are regulated by a combination of MKS mass-flow controllers and an automatic throttle valve. The operating pressure is maintained in the 15–200 mTorr range as measured by a MKS Baratron. The rf field is generated by means of a four-antenna low inductance flat spiral coil made of 1/4 inch copper tube and the power range is varied from 100 to 500 W. The coil is separated from the vacuum region across the quartz window. In between the quartz plate and the substrate holder, there is one circular gas ring, then a stainless steel grid and another gas ring with smaller diameter, placed sequentially. The grid is kept at floating condition, which actually confines the plasma within the quartz plate and itself, and protects the substrate from direct plasma interaction.

![Fig. 2.5 Schematic diagram of the inductively coupled plasma CVD chamber.](image)

### 2.3 Plasma Physics and Chemistry in PECVD System

Plasma can be generated by subjecting gases to very high temperatures or to strong electric or magnetic fields. In thermal plasma; electrons, ions, and neutral species are in local thermodynamic equilibrium. In non-equilibrium or “cold” plasma, the electrons
and ions are more energetic than the neutral species. Most of the glow discharges used for thin film plasma deposition is created by subjecting the gas to a radio-frequency (RF) electric field; they are non-equilibrium glow discharge plasmas. The electric field initially reacts mostly with the free electrons present in the gas. While the electric field also interacts with ions, these species initially remain relatively unaffected because of their much heavier mass. The accelerated electrons do not lose much energy in elastic collisions with gas species because of the large mass difference. In addition, these electrons do not lose much energy in inelastic collisions, such as excitation and ionization, unless their energies are higher than the relevant threshold energies (e.g., 11.56 eV for excitation and 15.8 eV for ionization in the case of argon). Inelastic collisions between high energy electrons and gas species generate highly reactive species, such as excited neutrals and free radicals, as well as ions and more electrons. By this mechanism, the energy of the electrons creates reactive and charged species without substantially increasing the gas temperature. The potential in the central region, or bulk plasma, is slightly positive with respect to the electrodes, due to the small surplus of positive ions. The plasma potential is the maximum value with which ions can be accelerated from the edge of the sheath towards the substrate, located at the grounded electrode. This may cause ion bombardment that may induce ion-surface interactions such as enhancement of adatom diffusion, displacement of surface atoms, trapping or sticking of incident ions, sputtering, and implantation. The bulk plasma is characterized by a constant potential. Electrons are expelled from the sheaths, so all ionization and dissociation processes must occur in the plasma bulk. Plasma light as a result of emission from excited molecules is only present in the plasma bulk, while the plasma sheaths are dark. The reactive species that are generated in the plasma have lower energy barriers to physical and chemical reactions than the parent species, and consequently can react at lower temperatures. The positive ions and the radicals reach the substrate by drift and diffusion, respectively, and undergo surface and subsurface reactions during deposition. In PECVD, these reactive species are utilized to form thin films at temperatures lower than those possible with thermally activated CVD. The charged species in the glow discharge may also affect the properties of the deposited films.
2.4 Role of Ions

Ion bombardment is either beneficial or has an adverse effect, depending on the deposition conditions. It is reported that ions can contribute up to 70% of the growth in PECVD deposition of microcrystalline silicon. Suppression of the ion energy is effective in improving the crystallinity, particularly at high growth rates. The ion energy depends on gas pressure, exciting frequency and the electrode configuration. The ion density in the plasma is determined by the electron density, whereas the kinetic energy of the ions is determined by the electron temperature. High excitation frequencies result in a greater electron density and a lower electron temperature. The average electron energy decreases with increasing frequency. In a diode type reactor, the frequency of the plasma excitation source has a direct correlation with the ion energy. Radicals are considered to be the main precursors for the growth of both amorphous and microcrystalline silicon in a PECVD deposition process. It is agreed from many reports that SiH₃ is the main precursor for the device quality films. Low lifetime radicals, higher silane radicals (Si₂H₅, Si₃H₈, etc.) and reactive radicals (SiH₂, SiH etc.) are considered a hindrance to microcrystalline deposition. However, it is mainly the ions which determine the final film quality. The ion flux density reaching the substrate is determined by the ion density in the plasma (electron density), whereas the kinetic energy of individual ions reaching the substrate is determined by the electron temperature in the plasma. In fact, it has been shown that with the same type of plasma it is only the presence or non-presence of ions (at the growing film), which determines whether it is amorphous or microcrystalline. However, it has to be emphasized that the presence of ions in the high frequency case would give rise to enhanced surface diffusion of impinging species, even at a low substrate temperature (Ts), which is a necessary condition for getting good crystallinity in the material. One of the methods for varying the ion bombardment is to choose the frequency of the power source generating the plasma. An earlier report in the case of VHF PECVD explained high crystallinity in the VHF process compared to 13.56 MHz samples as due to the presence of high energy ions in the latter case. This model is based on the criterion that the energy of the impinging particles on the growth surface must not exceed the threshold energy of defect formation. The plasma contains both silicon and hydrogen ions, but the effect of the latter is considered negligible. The peak of the ion energy distribution is a function of excitation frequency. As a result, the peak ion...
energies for excitation at 70 MHz or higher frequencies are around 14 eV, which is lower than the threshold energy of 16 eV for Si impact. In contrast to this, for the case of 13.56 MHz excitation, the peak of the ion energy value is around 45 eV. Another way of controlling ions which has been proposed is to use deuterium instead of hydrogen dilution. In PECVD, this has shown to improve the crystallinity and decrease the defect density. The reason suggested is that deuterium dilution leads to lower ion bombardment, due to a lower electron temperature in the plasma formed. This is attributed to the heavier mass of deuterium, which results in a lower electron loss rate.\textsuperscript{24}

The second method to manipulate the ion bombardment at the growing surface is through the design of the electrode configuration. An attempt to grow microcrystalline films by suppressing ions from reaching the substrate surface has shown promising results, as proposed by Veprek et al.\textsuperscript{25} A triode technique, in which there is a negatively biased mesh electrode between the plasma and the substrate, as proposed by Matsuda, is very effective.\textsuperscript{26} The effect of ion bombardment on the deposition is best observed in the case of the electron cyclotron resonance (ECR) CVD process. Here, due to remote deposition, the ion energy and flux at the substrate can be independently modified without affecting the plasma. De Boer et al. using the ECR process, observed that even when growing crystalline Si epitaxial layers on Si wafers, high ion bombardment (increasing bias voltage) led to an increase in the Raman line width and a decrease in the electron mobility in the film.\textsuperscript{27} Nozawa et al. observed in the case of ECR CVD that increasing the positive DC bias to the substrate improved the crystallinity.\textsuperscript{28} This was attributed to a decrease in the ion flux to the substrate.
2.5 References