INTRODUCTION
1.0. Introduction

Microelectronics has greatly revolutionized science and technology at its best. Microelectronics has had its significant impact on all walks of life. Be it communication, transportation, education, entertainment, space exploration, finance or any other field of human activity one has observed spectacular development in the last 50 years – primarily due to the use of microelectronic devices, circuits and systems.

This microelectronics technology gave birth to two important aspects.

a. Integrated electronics and circuits
b. VLSI design, tools and technology

The birth of microelectronics technique is traced back to 1947 when Bardeen, Brattain and Shockley invented the bipolar transistor at Bell Laboratory. The first major technology breakthrough towards integration of circuits came in 1958, with the invention of ICs. The key to this process was the use of lithography using SiO\textsubscript{2} as a mask, whereby selective introduction of impurities into wafer was made possible. As science progressed in silicon integrated circuits (SIC), a number of different logic families were developed. Thus, different levels of integration came into existence.

These developments were accompanied by major changes in design and fabrication process. We even came across metal-oxide-semiconductor (MOS) devices, on the other hand, held an inherent attraction for manufactures in that “silicon real estates” was much better utilized, as there was no intrinsic need for isolation. But this, MOS technology at that time had a big disadvantage with respect to quality of good active gate insulator.

Around 1962, different (oxidation) techniques for the growth of thin, high quality, active oxides were mastered and first MOS chips appeared in the market as medium scale integration era. This was possible only due to progress in fabrication technology i.e. **Thin Film Technology**.
Though this technology took its birth in 1838, it became relevant with respect to MOS devices since 1962 [1]. Thereafter, there has been a tremendous advancement in the field of IC (MSI, LSI, VLSI, and ULSI). The advances in thin film technology lead to a different fabrication philosophy and gave a major technological breakthrough in the field of ICs.

Microelectronics research is in large part driven by the demand for smaller components with enhanced performance. For capacitance components, which form the basis of many memory devices, the dielectric constant limits the degree of miniaturization- a limit that is now being approached for the materials currently in use. Now-a-days thin films of metals, oxides, alloys, nitrates and semiconductors have vast application potential in modern equipment and accessories resulting in tremendous advancement in technology.

1.1 Microelectronics- Thin Film Technology

Thin film technology is one of the fast developing fields in the area of scientific research. The development and study of these thin films and their properties have enhanced the advancement in other allied scientific fields like Solid State Physics, Optoelectronics, Plasma Physics etc.

The technology and understanding of films less than one micron thick have made tremendous advances in the last decade, primarily because of the industrial demand for reliable thin film micro electronic devices to fulfill the urgent needs of the sputnik-era. This progress has brought maturity and much scientific confidence in the use of thin films for basic and applied research.

Thin film technology is one of the oldest arts and one of the newest sciences. It was used to decorate copper and bronze statuary. After smoothening and polishing the metal surface, mercury was rubbed to it. Some metal dissolved in the mercury forming a very thin film that left the surface shiny and smooth [2].

Thin film science and technology finds application in many fields. Typical examples are a variety of active and passive micro miniaturized components and devices, solar cells, radiation sources, detectors, magnetic memory devices, cryotrons,
bolo meters, anti reflection coating, interference filters, surface mirrors, sunglasses, optical coating, super conductivity, tribology, space application, bio medical sensors, strain gauges etc. Though, materials have been prepared in the form of thin films, from many years its specific application is only available from the last three decades.

A thin film is a solid layer having a thickness varying from few Å to few micrometer. Based on the thickness, these films can be classified as (a) ultra thin (b) thin (or very thin) (c) comparatively thicker ones, greater than 1000 Å

A thin film is a two-dimensional structure at its microscopic appearance as its thickness is very small. Thus, a thin film can be scientifically defined as a thin two-dimensional material born out of an atom-by-atom or molecule condensation process. Condensation is generally activated from the vapour phase of the material. This makes it altogether different from its bulk counterpart. It is possible to prepare thin films with required properties and morphology for any specific applications by proper selection of deposition process and optimizing the deposition parameters.

Metallic and dielectric thin films finds application in metallic mirrors, anti reflection coatings, dielectric high reflecting mirrors, semi transparent mirrors, interface filters, dichroic mirror etc. Front surface aluminized mirrors are extensively used in optical instruments for visible and infrared regions. Optical semi-reflectors are used in interferometers, range finders and lasers. Anti reflective coatings will reduce the reflection and increase the transmission, as the energy has to be conserved.

High reflectivity mirrors find vast application in laser technology. With multi-layer deposition of thin films, it has become possible to produce mirrors, which approach nearly 100% reflectivity.

Band pass and band stop filters can be designed and fabricated by thin film deposition. Band pass filters designed to reflect the heat radiation and transmit only visible light are used in film projectors in order to reflect the heat away from the moving film.
Another widely used band pass filter is the cold mirror having a high reflectance for visible region throughout and a low reflectance to infrared spectrum. Evaporated thin films are widely used in ophthalmic industry for various purposes.

Thin films find use in microelectronics. The microelectronic devices are smaller, less expensive and more reliable in comparison with conventionally built circuits. In comparison with semiconductor circuits they are more flexible and permit the fabrication of components with closer tolerances. Passive components like resistors and thin film capacitors can be fabricated in a variety of ways by thin film deposition. Thin film technology allows for greater precision and miniaturization and is generally deposited on a glass or glazed ceramic substrate.

The resistive films are usually made of tantalum (nitride) and conductors are usually aluminium or gold. Pattern definition for resistors and conductor path can be achieved by depositing the films through the metal shields with proper apertures. Capacitors can be fabricated by depositing an insulating layer between two metal films or by oxidizing the surface of one film and then depositing the second film on top [3]. Better control over the film thickness makes it easy to fabricate resistors and capacitors with specific requirement. By choosing appropriate materials with the specific resistivity and electric permittivity, one can design a variety of micro electronic devices with the present day technology. Thin film photo conductors are used on photoconductive cells, image sensor arrays, television camera and electrostatic copying machines. These films are fabricated using CdS, CdSe, PbS, etc.

In some magnetic thin films, magnetization can be rotated and reversed at very high rates. This is used in fabrication of memory devices for computers. Thin film super conductor makes it possible to develop devices like SQUIDs and Josephson junction, which enables very low magnetic field measurements and high speed computing. On the energy front, thin film selective coating with a very high absorption in the solar spectral region and low emittance in the thermal IR region increases the efficiency of photo-thermal conversion. Development in photovoltaic conversion has been a result of thin film technology; materials like CdS, CuInSe have
been used to enhance efficiency of solar cells. Anti reflection coatings on conventional solar cells are proved to enhance its efficiency [4].

Depositing coatings of titanium nitride, carbon nitride, titanium carbide etc. has enhanced the performance of mechanical tools. On commercial front, watchcase, straps coated with TiN gives them a luster similar to that of gold [4].

Thin film technology allows for greater precision and miniaturization and is generally preferred when space is an important limitation. Thus, thin films have become an integral part of a variety of technologies from decorative to high technology devices. Thick films also find great use in printed circuit boards. Ideally functional properties of thin films should be equivalent or superior to that of the bulk material and those properties are determined easily. Thin film resistors, capacitors have many advantages over the conventional resistors and capacitors. In many aspects thin films have become an indispensable component in modern technology (VLSI / ULSI) [5].

**Thin film resistors:** Thin film resistors offer improved performances and reliability as compared with resistors of composition type eg. A high sheet resistance ($R_s=10-1000 \, \Omega/\square$) a high resistivity $\rho$ (30-160 $\mu \Omega /\text{cm}$) and a very low TCR (Temperature coefficient of resistance) with better performance and reliability are characteristics of thin film resistors such as hafnium, zirconium, titanium, manganese. However, it is in the area of integrated circuitry that thin film resistor has really come into their own [5].

**Thin Film capacitor:** For a given material, film thickness alone establishes the capacitance density. Dielectric films of capacitance density even up to $0.5 \mu \text{F} \, \text{cm}^{-2}$ can be fabricated [5]. Commonly used dielectric materials are evaporated SiO$_2$ and anodized Ta$_2$O$_5$. These thin film capacitors are being used in IC. The present trend is towards newer types of devices like monolithic, hybrid circuits, FET, MOS transistor, sensors, switching devices, cryogenic application, high density memory system for computer etc.
1.2 Methods of preparation of thin films

There are various methods/techniques for preparing thin solid films for research, development and production purposes. The deposition techniques for various thin films may be broadly classified under two categories.

1. Physical vapor deposition and [PVD]
2. Chemical vapor deposition [CVD]

Physical vapor deposition is a term that includes both evaporation and sputtering process. The objective of these deposition processes is to controllably transfer atoms from a source to a substrate, where film formations and growth proceed atomistically.

In evaporation, atoms are removed from the source by thermal means, whereas in sputtering they are dislodged from solid target (source) surfaces through impact of gaseous ions. In 1852, Grove observed metal deposits sputtered from the cathode of a glow discharged which was later observed by Faraday after 5 years with respect to fuse like metal wires in an inert atmosphere [1]. Higher deposition rates, better vacuum and cleaner environments for film formation and growth, good adherence to substrate, number of new alloy formation with good stoichiometry, an introduction to RF, bias and magnetron variants extended capabilities of sputtering to improve and progress at a fast rate. All these features help to promote the popularity of sputter-deposition [1].

Metal layers are deposited exclusively by PVD technique [1,2]. These layers are deposited or grown on a silicon wafer in normal SIC (silicon integrated circuits) technology. In PVD, metal is obtained in vapour form by some means, which is then transported to wafer surface where it nucleates and condenses. Only physical processes are used in the generation of vapour and no chemical processes are involved. Layers deposited by PVD are generally referred to as thin films and are usually of the order of 1µm.
Metal layers are commonly required in SIC for one of the three reasons.

(a) As a conducting wire for interconnections between different nodes of SIC being fabricated.
(b) As a contact metal to obtain ohmic contacts (or sometimes rectifying contacts).
(c) As a gate metal. (as a plate for a capacitor as in MOSFET gates / plate in DRAM structure).

The two commonly used PVD techniques are evaporation and sputtering. In both cases, the process is carried out in vacuum. Deposition techniques are thus classified as follows.

**DEPOSITION TECHNIQUES**

- **Physical methods**: Thermal evaporation, Resistive heating, Electron-bombardment, Flash Evaporation, Laser Evaporation, Arc Evaporation, RF heating, Exploding wire technique, Electron beam evaporation
- **Chemical methods**: Sputtering, DC Sputtering, -Bias Sputtering, RF Sputtering, Reactive Sputtering, Magnetron Sputtering, Reactive Magnetron Sputtering, Pyrolysis, Anodization, Polymerization, Electro-plating, CVD & Electrolysis
In evaporation, the material to be deposited is vaporized from source by the supply of some form of energy in a vacuum system normally evacuated to a pressure of less than $10^{-5}$ or $10^{-6}$ mbar. Here, heating of the material to be deposited is carried out directly or indirectly by different methods like resistive heating, electron beam heating etc. The theory of evaporation technique is based on the theory of vapour pressure, kinetic theory and thermo dynamics [6].

Resistive heating consists of heating the material with a resistively heated filament or boat, generally made of refractory metals such as tungsten (W), molybdenum [Mo], tantalum (Ta) and niobium (Nb) with or without ceramic coating. Crucibles of quartz, graphite, alumina, beryllia and zirconia are used for indirect heating. When multiple alloy and compounds are thermally evaporated, components may evaporate at different rates because of their different vapour pressures, and their different tendencies to react with support material and possible thermal decomposition of the parent material. These factors will obviously produce non-stoichiometry films. Thus, flash evaporation is useful for such applications.

In flash evaporation, a rapid evaporation of multi component alloy or compound that tends to distill fractionally may be obtained by continuously dropping fine particles of the material onto a hot surface so that numerous discrete evaporation occurs or a mixture of components in powder form may be fed into the evaporator [7,8].

Resistive heating and flash evaporation cannot be used to evaporate high melting point materials and to deposit pure films. In laser evaporation, high intensity of the laser beam may be used to heat and vaporize material by keeping the laser source outside vacuum system. In electron beam evaporation, any material can be evaporated virtually at any rate, by using powerful electron beams. This is called electron beam evaporation. This process is useful in the deposition of metals, alloys and compounds.
Another technique, which avoids heating of source material, is **Sputtering**. This process can be defined as “The ejection of atoms from the surface of a material (the solid target) by bombardment with energetic particles which can be charged / neutral”. If the ejection is due to positive ion bombardment, it is referred as “cathodic sputtering”. This process has been known since 1852.

- Here, ions are used for sputtering due to the fact that their energy and direction can be controlled by application of electric and magnetic fields.
- When compared to evaporation, adhesion of sputtered films is extremely good due to continuous charged particle bombardment on the substrate.
- Normally inert ions like argon are used to knock out atoms/molecules from target.
- Energies of the order of 0.6 to 1KeV are used to accelerate the ions in the vacuum. Sputtering is suitable for many applications and is replacing evaporation techniques.

Magnetron sputtering is used in semiconductor industry where high rates and low substrate heating are essential. Sputtering is a very well suited technique in the field of research and industrial thin film application as it is particularly well suited to applications that demand low deposition temperature and fairly high degree of uniformity over large substrate area.

### 1.3 Glow discharge sputtering

Sputtering is one of the most common methods used in SIC fabrication. Basically the process involves bombarding a target wafer with chemically inert ions like argon, knocking out atoms/ molecules from target. The first reference in this process was that of Groove [9]. Till 1950, studies were confined only to the Physics of ion bombardment. This process was given more importance when it was found that refractory, multi-component and insulating material could be deposited easily using this technique. The process of film deposition by sputtering is classified into a number of steps such as (a) ion production, (b) ion-target interaction, (c) sputtering of target material, (d) transport of sputtered material, and (d) nucleation.
1.3.1 Glow discharge process

Glow discharge can be obtained by applying a potential between two electrodes in a gas [10-12]. Most of the space between two electrodes is filled by a bright glow known as negative glow, which results due to excitation and subsequent recombination processes. Fig. 1.1 shows a typical glow discharge characteristic.

- Adjacent to the cathode is a dark region space known as cathode dark space. This corresponds to the sheath formed in front of the cathode (Aston and cathode (Crookes Hittorf)). There is also a similar sheath at the anode, which is too thin to clearly see.

- Positive column: It is the region of the discharge, which most nearly resembles plasma. It is found that when two electrodes are brought together, cathode dark space and negative glow are unaffected while positive column shrinks. As the two electrodes are brought together still closer, i.e. if this process continues, we will be left with negative glow and dark space adjacent to each electrode. The minimum distance between the electrodes should be twice the dark space thickness. If the distance is less, then the dark space is distorted and the discharge is extinguished [10].
In the discharge, electrons, ions and neutrons are present. Depending on these charges, the reaction at the cathode will be different from that at the anode.

**Fig 1.1**: Typical glow discharge characteristic
1.3.2 Cathode interaction

When a particle strikes a surface, one positive result is that an electron is ejected. The number of electrons ejected per incident particle is called secondary electron co-efficient / yield. In a dc sputtering process, the cathode is the target material, which is connected to the negative terminal. Since these sputtering targets are held at high negative potentials, secondary electrons are accelerated away from the target surface with an initial energy, which is equal to target potential. These secondary electrons help to sustain the glow discharge by ionization of neutral sputtering gas atoms, which in turn bombard the target and release more secondary electrons.

Secondary electrons are repelled at high velocity from the cathode and start to make collisions with neutral gas atoms at a distance away from the cathode corresponding to their mean free path. This leaves a dark space well defined. Since electrons rapidly lose their energy by collision, nearly all the applied voltage appears across dark space. The dark space is also the region in which positive ions are accelerated towards the cathode. Mobility of ions is less as compared to mobility of electrons. Thus, predominant species in dark space are ions. Acceleration of secondary electron from the cathode results in ionizing collision in the negative glow region.

The Faraday’s dark space and positive column are nearly field-free regions whose sole function is to connect electrically the negative glow to anode. Cathode reaction during sputtering process is shown in Fig.1.2.

The glow discharge is sustained mainly due to secondary electrons, and this is called as steady state discharge if there is a numerically equal number of ion-electron pair generation rate.

When a dc voltage is applied, the electric field is so strong that the major part of electrons travel will be straight across dark space along field lines. For each ionization, a new ion and new electron is formed i.e. when voltage is applied, a small current initially flow. This current is constant, because all the charges present will be moving.
Similarly when voltage is increased, after a certain potential, the ambient gas breaks down. A large number of ions and electrons are created in the gas. Sufficient energy is imparted on charged particles so that they produce more charged particles by collisions with (a) electrodes, and (b) with neutral gas atoms.

As charge increases, current also increase steadily, ‘Voltage’ is limited by output impedance of power supply. This is also called as Townsend discharge.

Fig.1.2: Cathode reaction during sputtering process
Eventually, an avalanche occurs; ions strike the cathode, release secondary electrons, which form more ions by collision with neutral gas atoms. These ions then return to the cathode, produce more electrons which in turn produce more ions.

**Ion neutral collision**

When the number of electrons generated is just sufficient to produce enough ions to regenerate the same number of electrons, the discharge is self-sustaining. In a glow discharge process, bombardment of ions on the cathode is not uniform throughout, but is concentrated near the edges of the cathode or at other irregularities on the surface.

As more power is supplied, bombardment increases, covers the cathode surface until a nearly uniform current density is achieved. As bombardment covers whole of the cathode surface, further increase in power produces both increased voltage and current density in the discharge. This region is called “Abnormal glow”.

Due to lighter mass, electrons move faster than ions. This leaves a positive ion sheath near the cathode. This leads to an increase in ionization current and space charge density. This positive space charge sheath is referred to as Crookes Dark Space. The thickness of this is inversely proportional to pressure. The positive ions strike the cathode and give rise to different effects depending on their energy.

**Ion-cathode interaction**

The ion-cathode interactions depend basically on the energy of the ions and cathode material. The typical possible reactions at the cathode due to ion bombardment may be [13]:

(a) The ion may be reflected

(b) The impact of the ion may cause the target to eject an electron

(c) The ion may get buried in the target, leading to the phenomenon of ion implantation

(d) The ion impact may be responsible for some structural re-arrangement in the target material
The ion impact may set up a series of collisions between the atoms of the targets (cascade collision process), possibly leading to ejection of one of the atom, which is called SPUTTERING.

### 1.3.3 Sputtering as a deposition process

The last mentioned process i.e. ejection of target atoms by the bombardment of ions is used for the deposition of thin films. The sputtering phenomenon has been known since 1852 [9]. Because of high pressure of gas used and high sensitivity to contamination in glow discharge sputtering, the technique at that time was termed “DIRTY”. But, later sputtering process has been subjected to numerous experimental and theoretical investigation and excellent reviews of subject have been published.

Stark [14] explained sputtering as a result of momentum transfer from bombarding ion to the atom in the target. This theory was amplified and further evidence of its validity was provided by Kingdom and Langmuir [15]. Von Hippel [16] discussed hotspot evaporation theory, which assumed sputtering to be only due to energy of the ions rather than their momentum. But this theory failed when Bariess [17] could not observe anodic sputtering by electrons. Later works also confirmed that the most applicable theory is that of momentum transfer and to date is being accepted.

According to the momentum transfer theory, the sputtering yield depends on the mass of the bombarding ion and its energy also. The sputtering yield is defined as the average number of atoms ejected from the target per incident ion which increases with the increasing energy and their mass.

During sputtering, several types of interaction may take place between sputtering ion and sputtered atom. One important parameter during this interaction is the sputtering threshold, which is defined as the minimum energy required for an incident ion for initiating sputtering process. This sputtering threshold depends on the mass of the impinging ion. Thus, for a given incident energy, maximum energy transfer to the target ion will takes place when the mass of the impinging ion and the target ion are equal [1].
A sputtering threshold exists between 5 and 25 eV for most metals, the lower limit being set by the sublimation energy. The yield increases very rapidly for energies beyond threshold, shows a small region of linear proportionality and then approaches saturation. But at very high energy, yield decreases because of increasing penetration depth and hence increasing energy losses below the surface, with the consequence that not all ejected atoms are able to reach the surface to escape. Though, these models explain the sputtering mechanism, in practice one has to consider that the sputtering target becomes a mixture of the original target material and bombarding species embedded in it. This may lead to errors in calculation of sputtering yield data [10].

1.3.4 Sputtering categories

Generally sputtering process is divided into four categories (a) DC sputtering (b) RF sputtering (c) Magnetron sputtering and (d) Reactive sputtering.

DC sputtering

In the typical sputtering process as shown in Fig 1.3, for thin film deposition [2] the material to be sputtered as a thin film is made the target i.e the target is a material from which a film is synthesized.

If the target is connected to the negative terminal of a dc or RF power supply, the target is known as cathode. Several kilovolts shall be applied to it. The substrate faces the cathode and is mounted on another electrode that may be grounded, electrically floating, biased positively or negatively, heated cooled or some combination of these.

As the target is kept at negative potential with respect to the anode, this configuration is called DC sputtering or diode sputtering. If the anode is left floating it can acquire certain potential from the plasma during deposition. Sometimes it may be deliberately kept at a potential. Then the process is called Bias sputtering. This process is also called as ion plating because the substrate, which is kept at negative potential, subjects the substrate to positive ion bombardment.
The target is normally shielded at the sides to avoid sputtering from undesired area. The cathode dark space decides the spacing between shield and target. Since the target is continuously bombarded with ions, the target must be cooled to avoid excessive heating. Since the substrate is bombarded with sputtered atoms, electrons, and neutrals it gets heated and has to be cooled. The entire electrode assembly is kept in a vacuum chamber with a provision of gas admittance for the sputtering process.
When a high potential is applied between the electrodes, the target being at the negative potential is bombarded by the positive gas ions leading to the ejection of target atoms, which fly off in random direction.

The parameters that influence the film deposition are the cathode potential and current density of ions on the target, both being functions of the sputtering pressure. The rate of sputtering depends on the flux of the incident ions on the target and sputtering yield. Choosing proper operating pressure is very critical both in terms of sustaining the discharge and the resulting film deposition.

At low pressure, the cathode sheath is wide and ions are produced far from the target. Low pressures require high cathode potential to sustain the discharge due to low density of gas molecules. This is due to mean free electron path between collisions which is large (less number of molecules) and electrons collected by the anode are not replenished by ion impact induced cathode secondary emission. Therefore ionization efficiencies are low and self-sustained discharges cannot be maintained. The potential applied to the cathode causes a rise in the temperature of the cathode due to the ion bombardment since 90% of the ion energy on the target is lost as heat in the solid material and only 5% is passed on to the secondary particles [18].

As the pressure is increased at a fixed voltage, the ions increase in number, the electrons mean free path is decreased, and thus a larger currents flow. Thus, ionization efficiency is high and hence rate of sputtering is high. But, if the pressure is too high, sputtered atoms undergo increased scattering due to collisions and are not efficiently deposited. Thus, optimum-operating conditions have to be chosen. In general, the deposition rate is proportional to power consumed, square of current density and inversely dependent on electrode spacing.

1.3.5 Problems in DC sputtering

Though dc sputtering is widely used in depositing thin films of various materials, it has certain inherent disadvantages. The basic disadvantage being that the sputtering target should be conducting. If the target is of insulating material, the applied voltage would give rise to an electrical field which is effective only on the
surface leading to space charge (ionization of gas would not be possible). Secondly, not all the sputtered atoms will have this energy, but will have a wide energy distribution because of collision with the atoms. Thirdly, the low deposition rates pose a major problem is depositing thick films using this technique. Operating the process at higher pressures enhances the rate of sputtering but the rates of deposition will be poor for the reasons discussed in the earlier section.

1.3.6 RF Sputtering

Sputtering with an alternating potential at higher frequencies offers solutions for the above-mentioned problems and this process is termed as RF sputtering and was first reported by Whener [19] in 1955. It is the process by which, films of any material can be deposited [20]. This versatility is not achieved without complications.

When ac signal is applied to the electrodes, (less than 50kHz) (dc sputtering), ions are sufficiently mobile to establish a complete discharge at each electrode on each half cycle. Here both electrodes alternately behave as cathodes and anodes. Above 50 kHz, i.e at higher frequencies, two important effects occurs:

(a) Electrons oscillating in glow discharge region acquire enough energy to cause ionizing collisions, reducing the need for secondary electrons to sustain the discharge.

(b) Secondly, RF voltages can be coupled through any kind of impedance so that electrodes need not be only conductors. This makes it possible to sputter any material. It eliminates the use of high potential required in a dc glow. Energy absorbed by an electron in RF field is proportional to square of the amplitude and hence independent of sign. Ions are not affected by the RF field because of their higher mass and lower mobility. The power is more commonly used because it is easier to maintain constant power in RF field sputtering circuit rather than voltage.

Here, one of the electrodes is grounded and essentially acts as a substrate holder. The other live electrode is connected to an RF generator. However, a frequency of 13.56 MHz with a power rating typically of order of kilowatts is normally used.
1.3.7 Reactive sputtering

In high frequency sputtering, stoichiometry of the deposited films deviates from that of target material [21]. So during deposition a certain amount of reactive gas should be present in system to achieve stoichiometry. Even in case where there is no target decomposition, the stoichiometry of the film is fixed and hence the composition of the film cannot be varied at will.

In reactive sputtering, thin films of compounds are deposited on substrates by sputtering from metallic targets in the presence of a reactive gas, which is usually mixed with the inert working gas (Argon). Sputtering in presence of reactive gas helps to control the composition of the deposited film and also helps to tailor its properties. The final result may be an alloy of the target metal doped with reactive element, a compound or some mixture of the two.

The most common compounds reactively sputtered (and reactive gases employed) are (1) oxides (oxygen) - Al$_2$O$_3$, In$_2$O$_3$, SnO$_2$, SiO$_2$, Ta$_2$O$_5$, ZrO$_2$, (2) nitrides (nitrogen, ammonia) - TaN, TiN, AlN, Si$_3$N$_4$, (3) carbides (methane, acetylene, propane) - TiC, WC, SiC, (4) sulfides (H$_2$S) - CdS, CuS, ZnS, and (5) oxycarbides and oxynitrides of Ti, Ta, Al and Si. Here, the nature of the reactive gas, its reactivity with target material and rate at which sputtered material atoms reach the substrate decides the composition of the film.

A good overview of the reactive sputtering process has been presented in the works of Holland and Campbell [21], Heller [22], Goranchev [23], Westwood [24,25].

1.4 Magnetron sputtering

When sputtering is associated with a transverse magnetic field it produces several modifications [26, 27] in the basic process. Magnetron sputtering is a type of sputtering in which magnetic field is superimposed on electric field between the target and substrate. The required magnetic field can be provided with either the permanent magnets or electromagnets. The magnets are well mated with the target with proper design. This is because of the influence of the magnetic field on the target-generated
secondary electrons.

Here, in magnetron sputtering, electrons within the dual field environment experience Lorentz force (ExH), in addition to the electric field force. The secondary electrons generated are trapped in the magnetic field geometry and they do not bombard the substrate and tend to move in a cycloidal path near the target obeying the Lorentz force relation as shown in Fig 1.4.

Fig 1.4: Effect of magnetic field on electron trapping

Thus magnetic fields prolong the electrons residence time in plasma and thus enhances the probability of ion collisions (ionizing). This leads to larger discharge currents and increased sputter rates. Thus applied magnetic fields have the desirable effect of reducing electrons bombardment of substrates and extending the operating vacuum range i.e. they do not contribute an increase in substrate temperature and radiation damage. This is called DC magnetron sputtering, which is advantageous in the deposition of thin films on low temperature substrates like plastics and surface sensitive MS/MOS devices.
Advantages of magnetron sputtering are:
(a) Ionization efficiency is increased when compared to other techniques.
(b) Plasma can be obtained at a much lower pressure i.e working gas pressure required to sustain the discharge is reduced.
(c) Magnetic field helps to increase sputter rate since it increases the velocity and therefore the momentum of the ions. Thus ionization efficiency increases and there by enhancing the deposition rates.
(d) Ions are produced close to the cathode, which is the ideal case for sputtering.
(e) DC magnetron sputtering is a potential process for large area industrial applications.
(f) Sputtering of atoms from substrate and walls of chamber is avoided as magnetic field applied is very close to target material which holds the plasma close to the target instead of substrate and increases ionization.

Different types of magnetrons sources like planar magnetron [26], cylindrical magnetron [28] and toroidal-conical magnetrons are developed depending on the need in specific applications. Magnetron sputtering is presently the most widely commercially practiced sputtering method only because of its high deposition rates.

1.4.1 Reactive magnetron sputtering

In reactive sputtering, thin films of compounds are deposited by sputtering from metallic target in the presence of a reactive gas usually mixed with inert working gas (argon).

Westwood has provided [24,25] useful ways to visualize the condition required to yield compound films. Sputter rates of metal decreases when compounds form on the target. The effect is very much dependent on reactive gas pressure and discharge current. Conditioning of target in pure argon atmosphere is required to resolve the pure metal surface and desired deposition states.

Depending on the operation condition, colour changes in films which shall appear due to variation in the stoichiometry. In the process of compound film
formation a small excess of either the metal or oxygen (or nitrogen) will not be rejected but will be included in the resultant film material [27].

The question of where compound formation takes place is essential to understand in the reactive sputtering process. Simultaneous conservation of energy and momentum requires the reaction to occur at solid surfaces either at the target or substrate. At very low reactive gas partial pressure and high target sputtering rate, it is essential that the reaction take place mostly on the substrate. However, when the rate of removal of the material from the target is far less than the rate of arrival of reactive gas atoms to the target, the compound formation takes place at the target also. This is termed as target poisoning [27].

In recent times, reactive magnetron sputtering has gained significant importance [27] for depositing hard optical coatings. The mechanism of reactive sputtering has been explained differently from time to time [25,29,30]. In recent studies [31,32] an anomalous behavior in glow discharge characteristics as a function of reactive gas pressure has been observed.

Planar magnetron sources usually are operated in Argon at a pressure of 1-10 mTorr and at cathode potentials of 300-700 V. Under these conditions, current densities can vary from 4-60 mA/cm$^2$, and the power densities are in the range of 1-36 W/cm$^2$.

For any optimum magnetic field shape and intensity, the current-voltage characteristics follow the relation,

$$I = KV^n$$

(1.1)

where I is the cathode current density, V is the cathode potential and n is the index for performance of electron trap. The more efficient the electron trapping in plasma, the higher exponent ‘n’.
1.5 Importance of the present study

Zirconium Nitride (ZrN) is one of the extensively studied transition-metal nitrides. The increased interest in both the application and the fundamental research of this material in the last decade stems from its remarkable properties. ZrN thin films have numerous applications due to their unique mechanical and refractory properties. Generally, ZrN exists in two different forms (a) stable metallic ZrN (b) metastable semitransparent insulating Zr$_3$N$_4$. ZrN, a compound which exhibits a good conductive metallic behaviour with low resistivity, good mechanical stability, wear resistance, and corrosion resistance has been used as good conductive films to provide new metallization schemes for gates, interconnections, ohmic contacts and Schottky contacts. These characters have made ZrN as a promising material for microelectronic, optics and VLSI/ULSI devices.

Transition metal nitride coating such as ZrN/TiN have been extensively studied for industrial applications such as hard coating [33,34], diffusion barriers in semiconductor technology [35,36,37], optical applications for heat mirrors [38-42] and decorative coating [43-46] because of their outstanding properties.

Many researchers have studied transition nitride coatings deposited by DC reactive magnetron sputtering, RF magnetron sputtering, ion plating, arc sputtering, electron-beam evaporation and dual ion beam sputtering. Among the methods, DC reactive magnetron sputtering is the most commercially practiced method because of its various advantages like high deposition rates on larger area substrates, control of the film composition, small substrate temperature rise during film deposition, films with better adhesion and thickness uniformity. It also minimizes target poisoning.

Varying the nitrogen stoichiometry in ZrN compound thin films, different colours like gold, brass and blue can be exhibited. Thus, gold like appearance of the compounds makes it move popular and more advantageous in commercial field. Therefore, ZrN can be a substitute for gold with better scratch resistance in every application. If by some means we can achieve this, then it can be one of the most likely efficient materials in thin film field as it is easy to fabricate, cheaper and can act as electrode for various devices in semiconducting field.
Very little work on optical, electrical, structural properties of ZrN thin films has been reported. Hence more effort should be put forth to understand these properties of ZrN thin films to realize their potential better in semiconducting field. Thus, this study is aimed at investigating different electrical properties of different devices using ZrN as an electrode.

Thus, the present investigation is aimed at
1. Optimizing process parameters in DC reactive magnetron sputtering to obtain good quality ZrN thin films.
2. Deposition of ZrN films using DC reactive magnetron sputtering on different substrates.
3. Studies on structural, electrical, optical and morphological characteristics of ZrN films.
4. Formation of metal-semiconductor contacts on different semiconductors and studying their electrical characteristics.
5. Fabrication of metal-oxide-semiconductor (ZrN/TiO$_2$/Si, Al/TiO$_2$/Si) devices using ZrN and standard Al as conducting electrode, then study their I-V, C-V, C-F characteristics and compare their results. Finally, metal-insulator-metal (MIM) device is fabricated and the electrical properties are studied.

1.6 Organization of the Thesis

The thesis is organized in a number of chapters.

- The second chapter gives a brief detail of different experimental techniques used in the present investigation.

- Chapter three gives details of balanced magnetron, application of ZrN thin films and optimized parameter of zirconium magnetron sputtering target and the investigations. It also gives details regarding review works on ZrN thin films along with the preparation and characterization of ZrN films (which
includes structural, electrical, optical behavior of the films deposited at room temperature and post annealed films).

- Chapter four deals with the fabrication and characterization of metal-semiconductor using ZrN as metal electrode on different substrates such as p-type Si, n-type Ge and p-type GaN.

- Chapter five is devoted to the fabrication and characterization of metal-oxide-semiconductor (MOS) and metal-insulator-metal (MIM) devices using ZrN as conducting electrode. The electrical studies (I-V, C-V and C-F measurements) of MOS and MIM structures are discussed. The results of MOS (ZrN/TiO$_2$/Si) have been compared by fabricating one more MOS structure (Al/TiO$_2$/Si) using Al as electrode.

- The sixth chapter details the summary of the results and the conclusions drawn from the present study and the scope for future work.

- Relevant references have been given at the end of each chapter.
REFERENCES

Chapter 1
Introduction
