Chapter 1

Introduction

This thesis reports on deposition and characterization of yttrium oxide ($Y_2O_3$) and yttria doped zirconia (YSZ) thin films. Both materials are refractory ceramics having important technological applications. The deposition of these thin films is carried out by capacitively coupled radio frequency (RF) plasma enhanced metalorganic chemical vapor deposition (MOCVD). Deposition of $Y_2O_3$ and YSZ coatings is also reported in literature using various other techniques but there are very few reports on deposition of these materials by RF plasma enhanced CVD process. Plasma as a deposition medium ensures uniform mixing of precursors and presence of highly energetic plasma species enables deposition of these coatings at lower substrate temperature. It can be seen from present work that $Y_2O_3$ and YSZ thin films deposited by process of RF plasma enhanced CVD are uniform, with good adhesion with the substrates and are nearly stoichiometric. The RF self bias on the substrate during deposition plays an important role in deciding the properties of the deposited films.

This chapter gives a brief introduction on the topic of thesis. A brief discussion on plasma, plasma sources and application of plasma sources is given. Various methods for deposition of thin films are described. A short introduction to RF plasma enhanced CVD and its advantages are given followed by discussion on yttria and yttria doped zirconia ceramics including their different phases and applications. Previous reports on deposition and characterization on these oxide coatings are also described in the section on literature review. A short description about the working principles of different characterization techniques is also included followed by thesis organization.
1.1 Plasma

Plasma is considered as the fourth state of matter which consists of ions, electrons and neutrals. The word ‘plasma’ is derived from the Greek word plásma meaning something that can be molded or fabricated. The flash of lightning bolt in the sky, fluorescent lamps, neon signs are some examples of plasma that we encounter in day to day life. The stellar interiors, atmosphere, gaseous nebulae consists of plasma.

The earliest work on plasma was reported by Langmuir, Tonks and co-workers in 1920’s. They were working on vacuum tubes that would carry large currents and hence had to be filled with ionized gas. Plasma can be defined as a quasi-neutral gas of charged particles and neutrals which exhibit collective behavior [1]. The separation of charges in the plasma can result into localized electric fields, but as the total number of positive and negative charges is same, overall the plasma is neutral; hence it is defined as a quasi-neutral gas. The motion of charged particles set up currents and fields which affect the motion of other charged particles which are at a distance. The constituents of plasma also show collective behavior.

The Saha ionization equation (1.1) gives the amount of ionization occurring in a gas at thermal equilibrium.

\[
\frac{n_i}{n_n} \approx 2.4 \times 10^{21} \frac{T^{3/2}}{n_i} e^{-U_i/kT} \tag{1.1}
\]

Here \((n_i)\) and \((n_n)\) are the densities (number per m\(^3\)) of ionized atoms and of neutral atoms, \(T\) is the gas temperature in °K, \((U_i)\) is the ionization energy of the gas and \(K\) is the Boltzmann’s constant.
From the above equation, it can be seen that at room temperature, the fractional ionization produced is of order of \( \frac{n_i}{n_n} \approx 10^{-122} \) which is considerably low. This fraction becomes considerable only when \( U_i \) becomes few times \( KT \) and the gas reaches plasma state [1].

A gas in thermal equilibrium has particles of all velocities and the most probable distribution of the velocities is known as Maxwell’s distribution. Thus at any given temperature there are some particles having energy higher than the average energy and these are responsible for ionization of gas through collisions with stray electrons and with other neutrals. Depending on pressure and density of species, the plasma can be broadly classified as thermal and non thermal plasma. In case of thermal plasma due to high pressure there are frequent collisions between the plasma species, thus equalizing the temperature of all plasma species. In this condition the plasma is in local thermal equilibrium (LTE). On other hand, in case of non thermal plasma, as the pressure is low, energy exchange between ions and electrons is less, resulting in two different temperature distributions for the ions and electrons and hence the plasma is in non-LTE. There are few exceptions like dielectric barrier discharge and atmospheric glow discharge, where the temperature distribution depends both on pressure and the distance between the electrodes (frequency of the power supply). Owing to high gas temperature associated with LTE systems, these systems are used for applications such as cutting, welding, spraying, etc. In such systems the plasma power density is in the range of 100 W/cm\(^3\) to above 10 KW/cm\(^3\) whereas non LTE systems are used for various processes such as thin film deposition, surface modification, etching and generally have power density in the range of 10\(^{-4}\) to a few tens of watt per cm\(^3\) [2].
The overall characteristics of plasma state is decided by the nature of precursors, pressure of gas inside the chamber, power fed into plasma, frequency of power supply used and the configuration of electrodes. Depending on these parameters different types of plasma discharge systems can be configured. Some non-LTE systems and their applications are discussed here in brief.

1.2 Types of plasma sources

1.2.1 Direct Current (DC) discharge

Here a DC electric field is applied between two electrodes that lead to acceleration of stray electrons. The accelerated electrons by way of inelastic collisions excite the atoms, ionizing them. The ions bombard the cathode, causing emission of secondary electrons. These electrons are responsible for sustaining the discharge.

![Figure 1.1: Schematic of DC plasma discharge](Ref-3)

The de-excitation within the visible region causes the discharge to glow. The DC discharge is characterized by different regions as shown in Figure 1.1 and there is change of electric...
field strength as one goes from cathode to anode. The region adjacent to cathode is characterized by a strong electric field called the cathode dark space; it arises due to the sheath region, where recombination of charges does not take place. Next is the negative glow region, it is the brightest region of the entire discharge as it has high density of both electrons and ions. When the distance between anode and cathode is relatively longer, two more regions known as the Faraday dark space and the positive column are present. In Faraday dark space, the electron energy and axial electric field is small. The positive column has low net charge density but sufficient electric field to maintain ionization. The anode glow is slightly brighter than the positive column. The anode dark space has negative charge density and a higher electric field as compared to the positive column. The DC discharge can operate over a wide range of pressures from 1 Pa to atmospheric pressure. The voltage used in the range 300 to 1500 V or more depending on the electrode configuration and the current is in the range of milli ampere [4].

1.2.2 Radio Frequency (RF) discharge

For sustaining the DC discharge, both the electrodes should be conducting. While using DC discharge for applications like thin film deposition of dielectric material, there will be a charge accumulation on the electrodes resulting in extinction of glow discharge. To overcome this barrier the electrodes are applied a varying electric field. The electrodes alternately change polarity and the accumulated charge can be fully or partially neutralized. The frequency used should be high enough so that the half the period of applied voltage is less than the time required for electrode to charge up. Otherwise there would be a series of short lived discharges with electrodes successively taking the opposite polarities instead of a quasi continuous discharge.
Figure 1.2: Schematic of (a) Capacitively coupled RF discharge (b) Inductively coupled RF discharge [Ref-4, 3]

The frequencies used are generally in radio frequency range of 1 to 100 MHz [5]. At these frequencies the electrons can respond to the high frequency field but the ions due to
their heavy mass cannot follow the field variations. While using radio frequency for creating discharge, two types of configurations are possible, inductively coupled plasma and capacitively coupled plasma. Inductively coupled plasma configuration leads to a high electron number density and low plasma potential that has advantage for semiconductor processing. Capacitively coupled plasma generation leads to a relatively low plasma density but high plasma potential. Further, the capacitively coupled plasma when coupled to a substrate immersed in plasma can be used for development of a self bias on the substrates. This has a very large number of applications in plasma based material processing. The generation of self-bias voltage on the substrates can be attributed to different response times of electrons and the ions to the applied RF field.

The self-bias DC voltage is formed when the electrodes have different size and a coupling capacitor is used between the electrode and RF power supply or when one of the electrodes is non conducting. The detailed mechanism of self bias generation is discussed in chapter-2.

1.2.3 Pulsed DC glow discharge

For these discharges, a pulse voltage of order of milli- or microseconds is applied to the electrode. A pulsed power supply can operate at higher currents and higher peak voltages for the same average power as in DC glow discharge, hence higher instantaneous ionization, sputtering is possible. Typically the peak voltage used is of the order of 500-800 V and pressure is ~100 Pa. In case of pulsed power discharges, the “power on” period is smaller than “power off” period. Because of less electrical power consumed, excess heating of the substrates is avoided. As compared to RF discharges, pulsed DC discharges have advantage that they do not require impedance matching network.
1.2.4 Atmospheric pressure glow discharge (APGD)

In this case a glow discharge is created between two electrodes (that may be covered by an insulating layer). A gas flow is maintained through the discharge volume and an alternating voltage of ~ 20 KV having frequency in the range of 1-30 KHz is applied. Distance between electrodes is few millimeter. The type of gas decides about the stability of the glow. For example, helium can give rise to stable discharge while with the use of gases like argon, oxygen and nitrogen, transition to filamentary glow discharge takes place. However operation in homogeneous glow discharge is possible by changing the electrode configuration. Main advantage is absence of vacuum condition; that makes the processing of high vapor pressure materials like rubber, textiles, biomaterials etc easier.

1.2.5 Dielectric barrier discharge (DBD)

This is similar to atmospheric pressure glow discharge. Basic difference between APGD and dielectric barrier discharge is that APGDs, are characterized by only one current pulse per half cycle while, DBDs consist of micro discharge filament of nanosecond duration. Two basic DBD configurations can be distinguished as the volume discharge and the surface discharge. In case of volume discharge, the system consists of two parallel plates; the micro discharges take place in thin channels spread randomly over the electrode surface. The surface discharge consists of number of surface electrodes on a dielectric layer and a counter electrode on the reverse side. There is no clearly defined discharge gap. The nanosecond discharge of DBDs is due to charge buildup at the dielectric surface within few nanoseconds after breakdown. This reduces the electric field at the position of discharge to such an extent that the charge current is interrupted. Due to the limited charge transport and
energy dissipation, heating of gas is avoided leading to utilization of electron energy in exciting and ionizing the atoms and molecules.

1.2.6 Electron cyclotron resonance (ECR)

These discharges are created by setting electrons in resonance with the applied microwave field owing to the interaction between the applied electric and the magnetic field. The frequency of gyration of charged particles around the magnetic field is independent of velocity of particles. The DC magnetic field is produced by one or more electromagnetic windings and varies in the axial direction. A linearly polarized microwave field is applied axially through a dielectric wall to the plasma. This field can be decomposed into two circularly polarized waves rotating in opposite directions, namely, left handed circularly polarized (LHP) and right handed circularly polarized (RHP).

![Figure 1.3: Schematic of ECR plasma discharge system][3]

The electric field of RHP wave rotates in the right handed direction around the magnetic field with a frequency $\omega$ while the electrons also gyrate in same manner with a frequency $\omega_e$. When the magnetic field is such that $\omega=\omega_e$, the electrons continuously gain energy along a circular path. Hence there is resonance between the microwaves and the electrons and
maximum power is absorbed. The LHP field on the other hand produces oscillating force whose time averaged value is zero and does not lead to any energy gain. However, the energy gained by electrons from the RHP wave is sufficient for the electrons to cause ionizing collisions. The ECR reactor essentially consists of two regions, the resonance region and the process region. The plasma flows along magnetic field lines from resonance region to the process region [2].

1.3 Application of plasma sources

With advances in modern technology plasma sources are finding a lot of applications in a variety of fields. The technologically important characteristic feature of non LTE plasma discharges is the role played by the active plasma species. Active plasma species promote reactions that are thermodynamically allowed but kinetically hindered or would normally require high temperatures, to occur at comparatively lower temperature. The active species produced by electron neutral collision includes neutral as well as charged reactive species. The neutral species include reactive atomic species, free radicals, light molecular fragments such as CH₂, heavy molecular fragments which can form complex compounds on the surfaces and promote branching and cross-linking of molecules, excited molecular states. The charged species include electrons, ions and molecular ions such as OH. The ions can be positive or negative. Positive ions are produced by ionization and charge exchange, while formation of negative ions is generally not possible under vacuum conditions and take place in atmospheric pressure plasmas by attachment of electrons. Use of plasma processing also contributes to reduction in pollutants and environmental contaminants. Further use of plasma in various processing also helps in increasing the energy efficiency.

Some applications of plasma discharge based processing are listed,
1.3.1 **Surface modification**

Interaction of plasma with surfaces has been put to various technological applications. These include,

1.3.1.1 *Plasma surface treatment or surface activation*

Plasma can be utilized for surface decontamination, sterilization, enhancing the surface energy, improving the adhesive and cohesive properties, altering the surface finish of the surface of the material. Specific applications of plasma surface cleaning include improving the wettability, wickability and printability of fibers, films and fabrics, dewaxing of wool or other animal fibers.

1.3.1.2 *Plasma ion implantation*

In this process energetic ions are produced by acceleration across a plasma sheath surrounding the substrate and implanted into the surface. Plasma ion implantation has been utilized for enhancing the wear resistance of drill bits. The corrosion resistance and pitting potential of aluminum and stainless steel is enhanced by plasma ion implantation.

1.3.1.3 *Sputter deposition of thin films*

Here energetic ions sputter atoms from target which are re-deposited as a thin film on a substrate surface. These sputter coated films have large industrial applications.

1.3.1.4 *Plasma enhanced chemical vapor deposition (PECVD)*

In late 1960s use of plasma for deposition of thin films in microelectronics industry was appreciated. In this process, active plasma species of the precursors react to form a thin film on the substrate. Films deposited by PECVD are finding applications in various areas like microelectronic industry, decorative and ornamental coatings, corrosion resistant coating, protective layer for optical components and in many other areas.
1.3.2 Plasma displays

Here, the discharge gas is usually a mixture of rare gases. The discharge forms plasma that emits light in visible and ultraviolet (UV) region of electromagnetic spectrum. In case of monochrome plasma displays, visible light can be used directly, while in case of color plasma displays, UV light is used to excite phosphor. The discharge can be operated in alternating current (AC) or direct current (DC) mode.

1.3.3 LASERS

Gas discharges can be used for making lasers. Here the gas at reduced pressure is contained within a glass discharge tube with mirrors at the end of the tube. Anode and cathode can be placed at both ends of the tube. The cathode can also have a hollow structure with anode rings at the end. Few examples are atomic lasers (He-Ne laser, copper vapor laser) and molecular lasers (CO₂, N₂, excimer laser).

1.3.4 Production of ozone

Ozone production is typical application of DBDs or high pressure gas discharges. Ozone can be generated from oxygen, air or from N₂/O₂ mixtures. First the O₂ molecules are dissociated by electron impact and by reaction with nitrogen atoms or excited N₂ molecules. Ozone is then formed by reaction of O₂ molecules with oxygen atoms. Major application of ozone is in water purification and pulp bleaching. In field of organic synthesis, applications include ozonation of oleic acids and production of hydroquinone, piperonal, certain hormones, antibiotics, vitamins, flavors and perfumes.

1.3.5 Environmental applications

Thermal plasma sources can be used for destruction of hazardous wastes. With the help of thermal plasma, organic waste can be destroyed with high efficiency, metals can be
recycled, heavy metals and low level radioactive materials can be vitrified. The non-thermal plasmas mainly used for environmental applications are high pressure discharges such as DBDs and pulsed corona discharges. Many harmful organic compounds are readily attacked by exciting species, free radicals, electrons, ions and UV photons generated in DBDs.

1.3.6 Biomedical applications

Plasma is used to enhance the biocompatibility of materials. Plasma sterilization of biological samples is gaining importance due to high efficiency of destruction of harmful microbes.

1.3.7 Particle sources

Since plasma consists of electrons, ions, excited atoms and radicals, it can be used as primary source of these particles [2].

1.4 Deposition of thin films

Thin films have been used since centuries from applications ranging from decorative coatings to protective layers. Thin films have left no field untouched and their applications can be widely seen in areas such as optics, magnetic materials, microelectronics, displays, biomedical applications, automobiles, construction, etc. By coating the base material, with thin film, a surface with properties significantly different from the bulk can be obtained. This provides the flexibility of choosing the base material according to requirements such as mechanical support, stability and cost. Thin films are routinely used to protect the materials from corrosion, excess heat, scratch, wear and harmful chemicals. Thin films with required optical and mechanical properties can greatly enhance the performance of the device in which they are used.
Various deposition methods have evolved over a period of time catering to different requirements. Selection of deposition process will depend on cost effectiveness, control of film thickness and microstructure, ability to acquire desired stoichiometry at required temperature, availability of suitable precursors and control on film substrate interface and defects created in the deposited films. The deposition techniques for thin films can be broadly categorized into two groups such as physical vapor deposition and chemical deposition methods.

1.4.1 Physical vapor deposition (PVD)

Physical vapor deposition is widely used for depositing thin films. This method involves evaporation of material to be deposited, transport of vapor onto the substrate and finally condensation of vapors on the substrate to form thin films. Vaporization of the material to be deposited is either achieved by thermal evaporation or by sputter deposition.

In case of thermal evaporation, the material to be deposited (also known as source) is heated above its melting point in high vacuum and the vapors then condense on the substrate. The evaporation of the source material can be achieved by various means such as resistive heating, electron beam, high power laser beam, pulsed laser beam or by RF heating.

In case of sputter deposition, the source material is bombarded by highly energetic noble gas ions in a vacuum chamber. The noble gas atoms hit the source material and eject atoms. These ejected or sputtered atoms are transferred to the substrate and condense to form thin films. Different types of sputter deposition techniques are DC sputtering, RF sputtering, magnetron sputtering and ion beam sputtering.
The disadvantage of physical vapor deposition technique is that it is a line of sight technique and can result in uneven thickness of the deposited films. Coating of complex shape structures cannot be done.

Molecular beam epitaxy (MBE) is another important PVD technique. MBE is a highly sophisticated technique for the growth of single-crystal epitaxial films by means of solid-source evaporation in an ultra-high vacuum environment (Knudsen effusion cells). The process provides high degree of reproducibility as well as flexibility and accuracy. Furthermore, it allows fabrication of intricate alloy and super lattice structures [6].

1.4.2 Chemical deposition (CD)

The CD process is based on a thermal decomposition of starting materials, on a heated substrate. Chemical reaction is an essential characterization of this method. Broadly on the nature of deposition medium used the chemical deposition technique can be classified into two groups- i) methods involving liquid phase reactions and ii) methods involving gas phase reactions.

i) Liquid phase chemical reaction methods

The liquid phase reactions methods are electrode less deposition, anodisation, liquid phase epitaxy, spin coating, spray pyrolysis, etc.

Some of the liquid phase reaction methods are discussed below,

a) Spray pyrolysis technique

This process involves generation of droplets from spray solution (atomization) and spraying it on the substrates. For this normally, air blast, ultrasonic or electrostatic techniques are used. After leaving atomizer droplets undergo physical and chemical changes while travelling through ambient conditions and are deposited on the substrate.
This method was introduced by Chamberlin and Skarman in 1966 for deposition of CdS thin films for solar cell applications. Since then, spray pyrolysis has been used for deposition of SnO\(_x\), InO\(_3\), PbO, ZnO\(_3\), ZrO\(_2\), YSZ, etc.

Advantages of this method are,

- Cost effective and easily performed.
- Complex geometry substrate can be coated.
- Uniform and high quality coating can be obtained.
- Coatings are reproducible and technique is useful for mass production.

**b) Spin coating**

This process is used to deposit uniform thin films on flat substrate. Generally a small quantity of coating material is applied on the center of the substrate, which is spinning at low speed or not spinning at all. The substrate is then rotated at high speed in order to spread coating material by centrifugal force. While fluid spins off the edges of the substrate, rotation is continued until desired film thickness is achieved. The applied solvent is volatile and it simultaneously evaporates. The thickness of the coating depends on viscosity and concentration of the solution. Higher the speed of spinning, thinner is the film. Spin coating is widely used in deposition of oxide layer using sol-gel precursors. This process is also used in photolithography to deposit layer of photo-resist material.

**c) Electrode less deposition**

In this method deposition of film is directly done by chemical reaction without application of any electrode potential. Chemical reaction can occur with or without catalyst. This method has been used to deposit several metals, e.g. Ni, Co, Pd, Au etc and oxide films.
The basic principle used here is to have controlled homogeneous precipitation of metal hydroxide and corresponding oxide film is prepared by annealing in air or vacuum [7]. Advantages of this method are,

- It is simple and economical technique.
- Does not require high temperature.
- Large area deposition is possible.

**d) Liquid phase epitaxy**

This method is used to grow semiconductor crystal layer from melt on solid substrates. This occurs at temperature well below the melting point of deposited semiconductor. The semiconductor is dissolved in melt of another material. At condition close to equilibrium between dissolution and deposition, deposition of semiconductor is fast and uniform. Most used substrates are InP, glass and ceramic. To facilitate nucleation and avoid tension in grown layer the thermal expansion coefficient of the film should match with that of the substrate.

**ii) Chemical vapor deposition**

The chemical vapor deposition (CVD) techniques are very popular for uniform deposition and coating of complex structures. Some of the CVD based methods are discussed below.

**a) Atomic layer deposition (ALD)**

In this technique, first the precursor is pulsed into the reaction chamber. Followed by its chemisorption on the surface of the substrate, here it forms a monolayer of the precursor on the substrate. For complete substrate-surface saturation the pulsing time needs to be determined. In the second step, the reactor is purged with an inert-gas to remove the un-
reacted precursor and in next step; the reactant is introduced into the reactor. The reactant reacts with the first precursor to form the desired material. In the last step the excess of the reactant and some by-products of the reaction are removed by subsequently purging with an inert-gas. The substrate temperature is a very important parameter in the ALD process. Advantages of the ALD technique are a precise film thickness control of the coatings and the possibility to coat substrates of different geometries resulting in conformal coverage. One drawback of this technique is the low growth rate (few Å per cycle), which would need long deposition times if thick films are required. Further, special types of precursors are required that possess a sufficient volatility combined with a high reactivity within the desired deposition process.

b) Metal organic chemical vapor deposition (MOCVD)

Metalorganic precursors are bulky molecules consisting of metal atom attached to organic ligands consisting of carbon, hydrogen and oxygen. The term MOCVD was coined by Manasevit who was the first to describe the use of metalorganic compounds for deposition of semiconductors in the year 1968 [8]. Precursors used for MOCVD should have high vapor pressure at low temperatures and higher decomposition temperature otherwise the precursor can undergo premature decomposition and as a consequence result into non uniform coating and blockages in the precursor delivery lines [9]. Besides this, the other desirable properties of required precursor are non toxic nature, air stability, easy handling and purity of deposition [8].

MOCVD technique has various advantages like low deposition temperature, good conformal coverage, uniform coating of the substrate, possibility of large scale production, ease of compositional control in complex films. Many different types of thin film coatings
such as oxides, carbides, borides, nitrides, silicides and chalcogenides can be deposited by MOCVD \[9, 10\].

c) **Plasma enhanced chemical vapor deposition (PECVD)**

Due to high internal energy state of plasma medium, deposition at lower substrate temperature is possible in PECVD compared to the conventional CVD methods. An early commercial use of PECVD technique was made in deposition of silicon nitride thin films used for the passivation and encapsulation of completely fabricated microelectronic devices. In presence of plasma reaction barrier is reduced and reactions occur at lower temperature hence excess heating of substrates is avoided. Due to reactive plasma species such as ions, electrons, neutrals, radicals a large variety of reaction pathways are available as compared to the thermal CVD techniques. The ions in plasma help in densification of films \[11\].

1.5 Deposition process used in present work

In the present work, capacitively coupled RF plasma enhanced metalorganic chemical vapor deposition technique is used for the deposition of yttrium oxide \((Y_2O_3)\) and yttria stabilized zirconia (YSZ) coatings. Precursor (2,2,6,6-tetramethyl-3,5-heptanedionate)yttrium known as \(Y(\text{thd})_3\) is used for deposition of \(Y_2O_3\) coatings while (2, 7, 7-trimethyl-3, 5-octanedionate) yttrium (known as \(Y(\text{tod})_3\)) and (2, 7, 7-trimethyl-3, 5-octanedionate) zirconia (known as \(Zr(\text{tod})_4\)) are used for the deposition of YSZ coatings.

The substrates are placed on the heated electrode connected to the RF generator through an impedance matching network. Generation of RF self bias voltage is an added advantage of capacitively coupled RF discharges. The bias level on the substrates during deposition is a crucial experimental parameter since it decides about the energy and flux of
ions bombarding the substrates. The detailed experimental procedure is discussed in chapter-2.

**Advantages of RF plasma enhanced chemical vapor deposition**

- Deposition of insulating coatings is possible which is not possible with DC plasma deposition system.
- The self generated DC voltage on the substrates act as a source of acceleration for the ions leading to uniform and dense film growth.
- Very high level of vacuum is not required for the operation.
- Unlike the microwave ECR plasma deposition process, this deposition technique is tolerant to minor pressure fluctuations.
- The system can be scaled up for industrial purposes.

1.6 Significance of yttria and yttria stabilized zirconia thin films

There are numerous technological applications of these coatings owing to magnificent properties possessed by yttria and yttria stabilized zirconia.

1.6.1 Yttrium Oxide

Yttrium oxide is also known as yttria. It is a refractory white ceramic with high melting point 2410 °C. Yttria has a bixbyite structure. Yttria was discovered in the year 1794 by Gadolin in a quarry located at Ytterby in Sweden. It has technologically important properties. It has large optical band gap (5.5eV) so it is transparent from near infrared to ultraviolet region of electromagnetic spectrum. \( \text{Y}_2\text{O}_3 \) has high refractive index (~1.7-2).
Yttrium oxide has high dielectric strength (~3.5 MV/cm), high dielectric constant (9-19) and good lattice constant matching with silicon [12].

i) Polymorphic forms of $Y_2O_3$:

Yttrium oxide exhibits four polymorphic forms,

a) Cubic $Y_2O_3$ (C-type): This is the stable structure found at ambient conditions with a lattice constant of ~10.6 Å. The structure is similar to CaF$_2$ structure. Each yttrium ion is surrounded by eight oxygen ions located at eight corners of cube.

b) Cubic Bixbyite structure: The distortion in cubic phase produces the fluorite structure, also called as the bixbyite structure with lattice constant ~ 5.2 Å, space group $T_\text{h}^7$ (Ia3). The C-type cubic phase transforms to bixbyite at temperature of 2308 °C. There are 32 yttrium and 48 oxygen ions in unit cell which can be visualized in form of 64 minicubes. Yttrium ions are located at centre of each minicube. Each yttrium ion is surrounded by six oxygen atoms with two of the eight cube corners vacant. As shown in Figure 1.4, there are two different sites, C$_{3i}$ and C$_2$ from where oxygen ions are missing. In case of site C$_{3i}$ the vacancies are arranged at the body diagonal while for C$_2$, the vacancies are arranged along the face diagonal [13]. A unit cell consists of 8 Y$^{3+}$ C$_{3i}$ sites (25%) and 24 Y$^{3+}$ C$_2$ sites (75%) with each cation 6-fold co-ordinated. Each yttrium atom is bonded to 6 oxygen atoms in C$_{3i}$ site by equal bond length of ~ 2.28 Å while each Y atom in C$_2$ site is bonded to 3 pairs of oxygen atoms with three different bond lengths such as 2.243 Å, 2.274 Å and 2.233 Å.
c) **Hexagonal structure**: The hexagonal (A-type) phase is generally reported at high temperature ~ 2325 °C and has lattice parameters a ~ 3.81 Å and c ~ 6.08 Å [15]. It belongs to the space group $P3_1/m1$. Here the yttrium ion is co-ordinated by 7 oxygen ions.

**d) Monoclinic structure (B-type)**: This phase generally occurs at high pressures having lattice parameters, a ~ 13.91 Å, b ~ 3.483 Å and c ~ 8.593 Å [15]. In this phase yttrium ion generally has 6 fold or 7 fold anion coordination. The cubic to monoclinic phase transition occurs at pressure greater than 13 GPa. This transition also occurs at high temperatures. Under high pressure, the cubic crystal will be compressed resulting in shortening of Y-O bond length. The cubic structure loses stability and a high density phase is formed. The covalent nature of bonds increases with decrease in Y-O bond length. The Y-O bond force constant increases by 20%, Y-O-Y by 25% and O-Y-O by 7% [13]. There is transformation from cubic to monoclinic phase, when the particle size decreases below 10 nm.
ii) Applications of Yttria

Yttrium oxide has been used for various applications ranging from corrosion and scratch resistant to optics. It is used as protective coating in reactive environments. As yttria is a refractory material with low neutron absorption, it can be used as structural material for nuclear reactors. It is used as component of sintering aids in silicon nitride, alumina and as a stabilizer in zirconia and in alumina-zirconia abrasives. Yttria is also used as high temperature refractory for continuous casting nozzles and as jet engine coatings. Due to the presence of oxygen vacancies, in yttrium oxide structure, it is used as oxygen sensor in automobile industry and for stabilization of zirconia [16].

Due to high refractive index of $Y_2O_3$, it is suitable as wave guiding material and a host matrix for doping of rare earth atoms. Eu-doped $Y_2O_3$ is a typical material well known as a red phosphor used in fluorescent lamps, cathode ray tubes, plasma display panels, field emission displays, etc [17, 18].

Refractive index and band gap are important parameters for optical waveguide devices. Higher value of refractive index enables confined optical transmission in the waveguide, thus increasing the efficiency of pumping and amplification [19]. As yttrium oxide is transparent from near infrared to UV region of electromagnetic spectra, it is also used as antireflection and protective coating for optical instruments. Yttrium-iron garnets are used as components in microwave radars for control of high frequency signal. With aluminum oxide, yttrium forms yttrium-aluminum garnet, which is used as solid state laser.

As the size of microelectronic devices is decreasing, search for materials with higher dielectric constant compared to silicon dioxide is gaining ground. Continuous scaling down of complementary metal-oxide semiconductor devices has pushed $SiO_2$ to its physical limits
due to its excessive direct tunneling current. Higher dielectric constant material will facilitate fabrication of layers without allowing leakage current to flow [20]. Due to its high dielectric constant and good lattice constant matching with silicon, Y$_2$O$_3$ is considered as potential candidate for replacement of SiO$_2$ as gate material in microelectronic industry [21]. Y$_2$O$_3$ is also used as an epitaxial buffer layer for deposition of high temperature superconductors such as YBa$_2$Cu$_3$O$_x$ on silicon. Properties required for the buffer layer are minimal chemical reaction between the two layers, relatively low electrical permittivity and a small lattice mismatch between silicon substrate and the deposited YBa$_2$Cu$_3$O$_x$ film [22].

1.6.2 Zirconia

The most commonly occurring natural form of zirconia is baddeleyite with a monoclinic crystalline structure which was first described in 1892 and named after Joseph Baddley. Zirconium oxide (ZrO$_2$) is a wide band gap (~5.1 eV) material with high dielectric constant (~18) and is chemically inert [23]. Zirconia undergoes phase transformation with temperature and the monoclinic form occurring under ambient conditions is transformed to tetragonal and cubic phases at higher temperatures.

i) Polymorphic forms of zirconia

Zirconia exhibits following polymorphic forms,

a) Monoclinic phase

It is the naturally occurring form of zirconia at room temperature and ambient pressure. This structure belongs to $P2_1/c$ space group with lattice constants $a \sim 5.156$ Å, $b \sim 5.191$ Å and $c \sim 5.304$ Å shown in Figure 1.5. It consists of four ZrO$_2$ unit cells with a density of 5.83 g/cc [16].
Monoclinic to tetragonal phase transition occurs at temperature of 1170 °C. The reverse transformation occurs at 900 °C and is associated with a 4 % volume increase and is martensitic in nature. The martensitic transformation is diffusion less and occurs by cooperative movement of set of atoms across an interface causing shape change and sound. Atoms frequently move less than an interatomic distance and hence nearest neighbors are maintained as far as possible during the change in crystal structure. Generally, there is a temperature hysteresis and polymorphism associated with martensitic transformation [25].

**b) Tetragonal phase**

This structure belongs to $P4_2/nmc$ space group with lattice constants $a \sim 3.64 \, \text{Å}$, $b \sim 3.64 \, \text{Å}$ and $c \sim 5.27 \, \text{Å}$ shown in Figure 1.6. It consists of two ZrO$_2$ unit cells. The tetragonal phase consists of three forms, $t$, $t'$ and $t''$.

The $t$ form is undistorted and stable structure. This form can transform directly to monoclinic phase. The $t'$ is metastable and has a distorted cubic structure. In this crystal lattice, alternate columns of oxygen ions are shifted in up or down directions by a small value ($\delta$). This distortion causes four oxygen atoms to move near zirconium atom and four oxygen atoms to move away from the zirconium atom. Each four oxygen atoms form tetrahedra
around the zirconia atom. For the $t^\prime$ form, the lattice parameters are same as that of cubic but the oxygen atoms are shifted in up and down direction alternately. Due to shifting of oxygen atoms, two types of tetrahedra are formed one elongated and one shortened giving two nonequivalent Zr atoms in the tetragonal structure. When the particle size of zirconia is small enough, tetragonal phase can be formed at room temperature. The tetragonal to cubic phase transition occurs at 2370 °C [26].

![Figure 1.6: Tetragonal ZrO$_2$ structure [Ref-24]](image)

c) Cubic phase

This form exists above 2370 °C. It has a fluorite structure (CaF$_2$) with space group $Fm\overline{3}m$ and lattice constant $a \sim 5.15$ Å. The crystal structure is shown in Figure 1.7.

![Figure 1.7: Cubic ZrO$_2$ structure [Ref-24]](image)
In this structure each zirconium atom is co-ordinated by eight oxygen atoms and each oxygen atom is tetrahedrally coordinated by zirconium atoms. The fluorite structure remains stable over a range of compositions from Zr$_2$O$_3$ to ZrO$_2$ [26].

**ii) Stabilization of zirconia**

The cubic ZrO$_2$ does not occur at room temperature due to smaller ionic radius (0.632) of $R_{Zr^{4+}} / R_{O^{2-}}$ than required (0.732) for the eight fold co-ordination [27]. The phase transformation with temperature is accompanied by volume change. This renders ZrO$_2$ coatings useless from technological point of view. To stabilize the high temperature phases at room temperature, zirconia is doped with larger cations to expand the lattice or by doping with lower valence cations, so that oxygen vacancies could be created or combination of both the effects takes place. The oxygen vacancies reduce the average co-ordination number and the oxygen sub lattice relaxes towards cubic symmetry. Some of the dopants used to stabilize zirconia are given below,

**a) Trivalent dopants**

The solubility of trivalent cations in ZrO$_2$ depends on the match of cation ionic radii and the similarity of cation and oxygen anion sub lattice between the dopants and ZrO$_2$.

The structure of rare earth oxides vary with the cation radius. The oxides of La, Ce, Pr and Nd have hexagonal structure. On the other hand, oxides with smaller cation radii such as Sm, Eu and Gd exhibit both monoclinic and cubic form. The interaction of dopants with ZrO$_2$ lattice is different for different dopants. For example, La$^{3+}$ has a strong tendency to segregate as pyrochlore La$_2$Zr$_2$O$_7$. Doping with Pr$_2$O$_3$, results in mixtures of tetragonal phases at dopant levels above 15 mol %. Doping with oxides of Nd and Sm results in structural distortion as compared to doping using Gd$_2$O$_3$. For oxide of Sc, there is a
tendency for segregation of rhombohedral $\beta$-phase above 10 mol %. $Y_2O_3$ has been found to be the best option for high temperature applications. $Y_2O_3$ as dopant imparts better mechanical and chemical stability to zirconia [28].

b) Divalent dopants

Alkaline earth metal oxide dopants such as CaO, MgO create two vacancies per cation. However, the dopant charge mismatch could create structural instability and phase segregation at high temperature.

c) Transition metals and $Al^{3+}$

$Al^{3+}$, $Fe^{3+}$, $Cu^{2+}$ and $Ni^{2+}$ are stable in $ZrO_2$. But on calcination above 800 °C, phase segregation occurs and m-$ZrO_2$ forms on cooling.

d) Tetravalent dopant

Tetravalent cations stabilize cubic phase by expanding the $ZrO_2$ lattice. So the dopant size must be greater than $Zr^{4+}$ (0.84 Å). Practically, due to low cost and toxicity, $CeO_2$ is preferred. Formation of cubic phase requires ~ 70 % $CeO_2$ while for tetragonal phase stabilization 30 % $CeO_2$ is required. Ce can be preserved as $Ce^{3+}$ through facile $Ce^{4+}/Ce^{3+}$ redox reaction that creates oxygen vacancies in $ZrO_2$ [27].

iii) Stabilized forms of zirconia

Variation of phases with dopant concentration of yttria is shown in the Figure 1.8. Depending on yttria content, various phases can be deposited. Below 3 mol % yttria, monoclinic phase is present. In the region from 2-6 mol % yttria content, partially stabilized zirconia is produced. Above 8 mol % yttria, fully stabilized zirconia is formed. Cubic like t” phase (a/c equal to unity) formed at ~ 8 mol % yttria which cannot be distinguished by XRD but have been identified from Raman spectroscopy and electron diffraction studies.
For yttria content between 15-40 mol %, mixtures of cubic $\text{Y}_2\text{O}_3$ doped $\text{ZrO}_2$ solid solution and segregated micro domains of $\text{Y}_4\text{Zr}_3\text{O}_{12}$ have been proposed. Crystallization of $\text{Y}_4\text{Zr}_3\text{O}_{12}$ has been observed for yttria content greater than 40 mol % [27].

**Figure 1.8**: Phase diagram of yttria stabilized zirconia [Ref 29]

**a) Single phase polycrystalline tetragonal ZrO$_2$**

Fine grain ZrO$_2$ (less than 0.5 µm) with small concentration of stabilizing dopant would contain up to 98 % of metastable phase. For this phase, strength increases with decrease in content of monoclinic phase. It has been found that particles with grain size less than 0.3 µm exhibit highest strength and toughness. The grain size effect is controlled by concentration and type of dopant ion, that determines degree of tetragonality (lattice ratio c/a is greater than 0.1) and thermal expansion anisotropy (c versus a direction). In general high tetragonality results in a less stable material. Anisotropic thermal expansion for c and a axis can influence residual strengths in tetragonal grain. Higher residual stress can lower
nucleation stress threshold for tetragonal to monoclinic transformation in presence of strain energy. At similar grain size and dopant concentration yttrium is a stronger stabilizer than cerium and titanium. [30]

b) Partially stabilized zirconia (PSZ)

Doping zirconia with 3-5 mol % yttria results in mixture of monoclinic and tetragonal phases. Phase constituent studies of zirconia doped with yttria in the concentration range of (2.8-4.0 mol %) indicate two tetragonal zirconia phases with varying degree of tetragonality. Both phases have slightly distorted fluorite structure and differ in the ratio of their lattice parameters. For the t-phase, the c/a ratio ~ 1.1014-1.015 while for other t’-phase the c/a ~ 1.004-1.005 [31]. The yttrium rich t’ is not transformable while lower yttrium content undergoes martensitic transformation to monoclinic phase under mechanical stress.

Milovichi et al. [31] have reported that micro hardness does not change for the different tetragonal phases but there is noticeable decrease in fracture toughness with increasing dopant concentration due to decrease in volume fraction of transformable tetragonal phase. PSZ has high wear and scratch resistance. It has good impact resistance. It is resistant to corrosion, chemical attack and thermal shock. PSZ has high melting point and low thermal conductivity. On application of external stress, the tetragonal phase transforms to monoclinic phase and there is ~ 4 % volume increase. This produces compressive stress in the film, arresting crack propagation and thus imparts fracture toughness to the material.

c) Fully stabilized Zirconia (YSZ)

Zirconia can be stabilized in cubic form at room temperature by addition of ~ 8 mol % Y₂O₃. Some Zr⁴⁺ ions are replaced by Y³⁺ ions. As Zr has valency +4 and Y has valency +3 so vacancies are generated for charge compensation. One vacancy is generated for every
two yttrium ions. YSZ is a solid solution in cubic fluorite structure with yttrium and zirconium on face centered cubic cation lattice (Figure 1.9). The oxygen ions and vacancies are located on simple cubic anion lattice. In cubic fluorite structure, each cation is in center of cube of eight anions and each oxygen ion or oxygen vacancy is in center of cation tetrahedron. The vacancies become mobile at high temperature ~ 600 °C and act as ion conductor. Cubic YSZ has low thermal conductivity, is chemically inert and brittle [32].

![Figure 1.9: Structure of YSZ](Ref-33)

**iv) Applications of stabilized forms of zirconia**

The stabilized forms of zirconia have numerous technological applications.

*a) Applications of PSZ*

PSZ is used as coating for cutting tools and dies. It is used in manufacture of knives, scissors and blades. As PSZ is wear resistant, it is used for bearings and linings, in pump parts and in grinding media

*b) Applications of YSZ*

YSZ coatings are used as refractory in jet engines. As it is hard and chemically inert, it is used as tooth crown. YSZ is used as thermal barrier coating in gas turbines. As YSZ is
electro ceramic, it is used as solid electrolyte in fuel cells and as sensor to determine oxygen content in exhaust gases and to measure pH value in high temperature water. Cubic zirconia is used in jewellery. YSZ doped with rare earth materials can act as a thermographic phosphor and luminescent material. It is used as a high precision alignment sleeve for optical fiber connector ferrules [32].

1.7 Review of Literature

1.7.1 Yttria based thin films

Due to the immense technological applications of Y$_2$O$_3$, research and development on Y$_2$O$_3$ coatings was carried out by various groups. A large variety of deposition processes have been used to deposit yttrium oxide. Literature indicates that Y$_2$O$_3$ have been deposited by spray pyrolysis [34], thermal oxidation [21], thermal CVD in atmospheric pressure [35], low pressure CVD [36], plasma assisted CVD [37], metal organic CVD [22], molecular beam epitaxy [38], atomic layer deposition [39], electron beam evaporation [40], ion beam assisted deposition [41], pulsed laser deposition [42,43] and radio frequency sputtering [44,45]. Metal-organic precursors have been extensively used for deposition of Y$_2$O$_3$ thin films. Deposition of Y$_2$O$_3$ thin films by Y(thd)$_3$ metal-organic precursors have been reported earlier by different researchers [22, 46, 37, 47, 48, 49]. G. Alarcon-Flores et al. [12] studied the decomposition characteristics of Y(acac) precursor. Stoichiometric Y$_2$O$_3$ deposition with less carbon contamination was reported by T. T. Van [50] by ALD process using Y(thd)$_3$. There have been few reports on deposition of plasma enhanced MOCVD of yttrium oxide thin films. Durand et al. [47] have used pulsed liquid- injection plasma enhanced MOCVD and studied the interface formation. Varhue et al. [22] utilized ECR plasma source and reported
deposition of (111) oriented Y$_2$O$_3$ films while Barve et al. studied the effect of deposition parameters on the Y$_2$O$_3$ thin films deposited by ECR plasma source [48, 51]. There are very few reports on RF plasma enhanced MOCVD of Y$_2$O$_3$ thin films. For e.g. Niu et al. deposited yttrium oxide thin films using two different precursors, [Y(HFAA)$_3$] and Y(thd)$_3$ by RF plasma enhanced MOCVD and studied the interface formation [37]. In this thesis RF plasma enhanced MOCVD of Y$_2$O$_3$ thin films is reported. This includes characterization of coatings and correlation of coating properties with the plasma process parameters.

The structure of yttrium oxide was studied both theoretically as well as experimentally by various research groups. The lattice parameter and dislocation density of undoped yttrium oxide single crystal was determined by F. Hanic and co-workers [52]. Vibration spectroscopy was extensively studied and assignment of infrared spectra [53] and Raman spectra [54] was done. The presence of oxygen vacancies in bulk affects the electrical and mechanical properties of Y$_2$O$_3$. The study of oxygen vacancies in case of epitaxial grown Y$_2$O$_3$ thin films was carried on by A. Travlos et al. [55] and it was reported that the oxygen vacancies order in a super structure. The oxygen deficiency results in decrease in electronic gap by 0.8 eV.

The effect of variation of deposition parameters on the properties of Y$_2$O$_3$ thin films were studied by different research groups [22, 56]. Cheng et al. [57] varied the O$_2$ pressure and temperature while depositing Y$_2$O$_3$ by pulsed laser deposition and found that the crystallinity improved with increase in substrate temperature. The structural transition from monoclinic to cubic phase was observed with increase in temperature by M. -H. Cho et al. [58]. Yttrium oxide has bixbyte structure so surface minimization favors growth along (111) direction. It was observed that there is change in orientation from (111) to (100) direction.
with oxygen partial pressure. The accommodation of internal stress was stated to favor growth along (100) direction [59]. Effect of deposition parameters on morphology and preferred growth direction was studied by other groups also [60, 61]. Tustison et al. [62] have reported studies on stress developed in Y$_2$O$_3$ thin films. The effect of post deposition annealing on the structure and optical properties of Y$_2$O$_3$ thin films has been reported stating that there is reduction of defects and enhancement of refractive index as a result of high temperature annealing [19].

The optical and structural properties of Y$_2$O$_3$ thin films were studied extensively by several researchers [12, 44, 63, 43]. The high refractive index and transparency over a wider range (near IR to UV) makes Y$_2$O$_3$ a useful material in field of optics. Rare earth ion doped luminescent materials have acquired significance. Luminescent materials have applications in many devices like lasers, waveguides, fiber-optic amplifiers, X-ray imaging, bioimaging, field emission, electroluminescent displays, etc. Y$_2$O$_3$ has high melting point, high thermal conductivity, good chemical stability which makes it a favorable candidate to serve as a laser material [18]. It is beyond doubt that the yttrium oxide thin films are promising for optical applications such as phosphors or laser waveguides. Y$_2$O$_3$ has been doped with rare earth elements such as Eu, Er, Tb, etc for these applications. Thullium doped Y$_2$O$_3$ was reported to produce high fluorescence intensities [64]. It is known that nanoparticles exhibit exotic properties that are not seen in the bulk material so their study acquires significance both from fundamental as well as technological point of view. Ramana et al. have reported enhancement in optical properties of nanocrystalline thin films as compared to the microcrystalline films [65]. Room temperature ferromagnetism has been reported in Y$_2$O$_3$ nanoparticles [66]. Tb-doped Y$_2$O$_3$ nanoparticles show increase in photo luminescent (PL)
efficiency as compared to the bulk [67]. However, for achieving better (PL) efficiency and better resolved (PL) spectra, the dopant location and distribution in the host matrix needs to be precisely controlled.

Due to scaling down of microelectronic devices, alternate high dielectric constant materials to replace SiO$_2$ were sought and research on Y$_2$O$_3$ as a gate material gained ground. Due to its high dielectric constant, high electrical strength and good lattice constant matching with silicon, Y$_2$O$_3$ proved to be a suitable candidate for this purpose. However, the formation of interfacial SiO$_2$ layer proved to be detrimental and reduced the effective dielectric constant. Efforts were made to understand [47] and reduce formation of SiO$_2$ layer. For e.g Niu et al. pre-nitrided the silicon surface before deposition of Y$_2$O$_3$ [37], Durand et al. reported that high flow of reactive species would suppress the formation of SiO$_2$ interlayer [47]. While Chang Ki Lee and Hyung –Ho Park have reported that forming an interfacial yttrium silicate layer reduces the SiO$_2$ layer formation and improves the electrical properties [68].

1.7.2 Zirconia based thin films

As fully and partially doped zirconia have numerous technologically important applications, extensive research has been conducted by different groups. Several deposition methods have been reported in the literature for the deposition of Y$_2$O$_3$ stabilized ZrO$_2$ namely DC magnetron sputtering [69], pulsed laser deposition [70], co-precipitation method [71], plasma CVD [72], electron beam evaporation [73], metal-organic chemical vapor deposition (MOCVD) [74].
The type of dopant and its concentration effects on lattice parameter, average crystallite size were studied by Abbas et al. [75]. MOCVD of YSZ films with reduced carbon contamination was reported using β-diketonate precursors [76].

Besides dopant, other experimental parameters will also influence the deposition of yttria doped zirconia thin films. Effect of variation of deposition parameters on the film properties have been studied by Stamper et al. [77]. They studied the texturing of YSZ thin films as a function of substrate temperature and also effect of oxygen annealing on the crystal structure of the deposited films. Qiling et al. studied the influence of oxygen partial pressure and growth rate on refractive index of YSZ thin films [78]. Hartmanova et al. observed transition from amorphous phase to cubic phase with substrate temperature but could not observe monoclinic or tetragonal phase. They also measured the ionic conductivity and activation energy and found it equivalent to that reported for the bulk [73]. The effect of substrate temperature on optical and structural properties was studied by Boulouz et al. and they reported that substrate temperature has greater influence on pure ZrO₂ as compared to yttria doped films [79]. IR analysis was carried on nonstoichiometric yttria stabilized zirconia at elevated temperatures by Liu et al [80]. IR transmission spectra of pure and doped ZrO₂ nanoparticles with different particle sizes were measured by Z. Qian et al. [81] and observed that nanosized particles show broad and flat absorption bands. Detailed infrared and Raman studies were made on ZrO₂ doped with different yttria concentrations [82]. XPS studies were carried by D. Majumdar et al. and observed yttria segregation at the surface of tetragonal phase [83].

EXAFS studies were carried in detail by Ping Li et al. They studied the characteristic local structure, effect of yttrium oxide dopant on zirconium oxide structure [84, 85]. They
have reported that Zr has different local structure in different phases, but the Y local structure remains the same. XANES and EXAFS study was carried in case of nanocrystalline YSZ to study the grain boundaries [86]. Martensitic phase transformation in partially stabilized zirconia imparts fracture toughness to the material. A. G. Evans et al. correlated the toughening associated with martensitic transformation with particle size distribution, chemical free energy and strain [87]. Technologically important properties of zirconia based films were studied by various research groups. S. Novak et al. have studied the structural changes caused by wear process and arrived on the conclusion that transformation of zirconia is the major wear determining factor [88]. M. S. Miller have reported the correlation of properties of PSZ with the deposition parameters [89] K. Miyazawa et al. have observed that oxidation resistance of zirconia thin films coated on stainless steel increases by increasing the yttria content [90]. S. Heiroth et al. observed that amorphous YSZ layers exhibit higher optical transmissivity, lower bandgap energy, reduced hardness and elastic modulii as compared to the crystalline YSZ [91]. Low thermal conductivity of YSZ is utilized for fabrication of thermal barrier coatings. Thermal barrier coatings are used to thermally insulate turbine engine blades from high temperature combustible gases within the gas turbine. These coatings enable higher engine operating temperature, higher thermal efficiency, higher cost effectiveness and longer lifetime for the turbine. Extensive work has been carried out on YSZ for use as thermal barrier coatings [92].
1.8 Characterization techniques used

The deposited films are characterized by various characterization techniques. Brief discussion about the characterization techniques used during the course of these investigations is given in this section.

1.8.1 Infrared (IR) Spectroscopy

IR spectroscopy is a powerful analytical tool for structural and compositional characterization of materials (both organic and inorganic) and is widely used in areas like material science, catalysis, medicine, biochemistry, forensic science etc. Change in vibrational modes of atoms in a molecule, are greatly influenced by the mass of atoms, their geometrical arrangement and strength of chemical bonds. A molecular vibration is IR active only when the interacting IR radiation causes modulation of molecular dipole moment. Vibration spectra will be observed only in heteronuclear diatomic molecules, as homonuclear molecules have no dipole moment. IR spectroscopy encompasses a spectral region from red end of visible spectrum (12,500 cm\(^{-1}\); 0.8 µm) to microwave (10 cm\(^{-1}\): 1000 µm) of the electromagnetic spectrum. Based upon both application and instrumentation it is conveniently divided into near IR (12500 cm\(^{-1}\) to 4000 cm\(^{-1}\)), mid-IR (4000 cm\(^{-1}\) to 400 cm\(^{-1}\)) and far IR (4000 cm\(^{-1}\)to 10 cm\(^{-1}\)) regions. The most fundamental molecular vibrations occur in mid-IR making this region richest in chemical information while overtones and combination of fundamental vibrations especially those involving hydrogen appear in the near-IR. On the other hand far IR region pertains to vibrations involving heavy atoms, lattice modes of solids and some rotational absorption of small molecules.
Currently most modern IR absorption instruments use Fourier Transform techniques with a Michelson interferometer. Unlike conventional IR instruments, in FTIR instrument all the frequencies are used simultaneously to excite all the vibration modes of different types of bonds/linkages present in the sample. This reduces the experimental time considerably. With these advantages measurement of transmission, reflection or even emission spectra has become significantly faster and with higher sensitivity than before.

1.8.2 X-ray photoelectron spectroscopy (XPS)

XPS is a non destructive surface analysis technique probing a depth of ~10 nm of the sample. It is one of the three widely used electron spectroscopy techniques where X-ray photons, typically of the range 1200-1500 eV, knock out the electron from solid surfaces. The kinetic energy of the photoelectrons is measured with a suitable analyzer and detector. The kinetic energy of the emitted electron is given by equation no.(1.2), where $E_k$ is the measured kinetic energy, $h\gamma$ is the energy of X-ray, $E_b$ is the binding energy of the electrons in the solid and $\phi$ is the work function of the spectrometer (order of 4.5 eV).

$$E_k = h\gamma - E_b - \phi \quad (1.2)$$

The X-ray source and spectrometer work function values are incorporated in the data acquisition software and finally the spectrum is displayed as binding energy against photoelectron peak intensity. The energy values of the photoelectrons are characteristic of elements. The quantification of elements is possible by measuring the peak area corresponding to the element and knowing its sensitivity factor. The binding energy and shape of the photoelectron peak can be analyzed precisely to find the chemical states of elements and their quantitative composition within the electron parameter depth of the solid.
It is found that photoelectron intensity depends on incident X-ray flux, number of atoms of the element of interest, cross-section of ionizing level, probability of no-loss escape of electrons, acceptance solid angle and detection of the instrument.

![Figure 1.10: Schematic of XPS set-up [Ref 93]](image)

**1.8.3 Atomic force microscopy (AFM)**

AFM measures the topography of conductors, semiconductors and insulators with a force probe located within few Å of the sample surface. The main components of an AFM instrument are probe, piezoscanner and detection system. The probe used in AFM consists of a flexible cantilever and sharp tip. Depending on the sign of electrical voltage applied the piezoelectric scanner expands or shrinks, which is proportional to the voltage. The scanning is carried out by moving the sample under the tip by means of piezoscanner.
There are mainly two types of AFM modes, namely, the contact mode and semi-contact/tapping mode, which are used for imaging the samples. In the contact mode, the force between the probe tip and substrate is repulsive and it is within the range of $10^{-8}$ to $10^{-7}$ N. The contact mode can obtain higher atomic resolution than the other modes but it may damage a soft material due to excessive tracking forces applied by the probe on the sample. Therefore soft cantilevers are used. In tapping mode the main interaction force between the probe tip and the sample is the Van der Waal’s force and it is in the range of $10^{10}$ to $10^{12}$ N. Here, cantilever oscillates in the attractive region and its oscillation frequency gets modulated depending on the sample surface features. The probe tip is 5 to 150 nm above the sample surface. The resolution in this mode is limited by the interaction with the surrounding environment. In the tapping mode, rigid cantilevers are used. Use of sharper probe results in images with good resolution. Three dimensional surface imaging and determination of surface roughness is possible with AFM.
1.8.4 X-ray diffraction (XRD)

X-ray diffraction techniques are fundamental in understanding the structure of material under study. Better understanding of the structure further opens pathways for analyzing the properties exhibited by the material. X-ray diffraction principle is governed by Bragg’s law (equation-1.3) which states that when X-rays of wavelength ($\lambda$) is incident on the surface with the interplanar spacing ($d$) of order of 1-100 Å, constructive interference of the diffracted rays gives rise to maximum intensity at certain angle ($\theta$) which is called the Bragg’s angle.

$$n\lambda = 2dsin\theta \quad (1.3)$$

Where, $n$ is integral multiple of $\lambda$

Generally for study of bulk material, $\theta$-2$\theta$ (Bragg-Brentano) reflection geometry is used. Here the incidence angle is equal to the diffracted beam angle with respect to the sample surface. The device configuration enables high intensity diffracted beam from any particular set of crystalline planes to be focused on a slit in front of rotating detector. However, for greater angle of incidence, the X-rays can penetrate depths of few to several hundred micrometers inside the material. In case of thin film analysis, the beam penetration depth can be greater than the thickness of the film resulting in diffraction pattern dominated by the substrate peaks. By using grazing incidence configuration, the XRD measurements become more sensitive to the surface region of the film and the substrate contribution is minimized. In case of grazing angle X ray diffraction (GIXRD), a parallel monochromatic X-ray beam is incident on the sample at a fixed angle less than 2-3 degree and diffraction profile is recorded by detector scan only. By using this technique information regarding thickness, phase, change in composition with depth and microstructure can be obtained.
1.8.5 Spectroscopic Ellipsometry

Ellipsometry was first developed by Drude in the year 1887. Ellipsometry is an optical technique that measures change in polarized light upon reflection or transmission from the sample. When linearly polarized light is reflected from the sample, the perpendicular (s-) and parallel (p-) components experience a different attenuation and a phase shift according to the Fresnel equations. Therefore the reflected light is elliptically polarized as seen from Figure 1.12. This technique measures the amplitude ratio ($\Psi$) and the phase difference ($\delta$) between (p-) and (s-) polarized light waves. When ($\Psi$) and ($\delta$) values are obtained by scanning the wavelengths generally in UV/visible region, variation of optical properties is obtained. Measurements in IR region have also been reported. Complex refractive index ($\rho$) for the sample is given by equation,

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\delta}$$  \hspace{1cm} (1.4)

Where $r_p$ and $r_s$ are the complex Fresnel reflection coefficients of the material for the p- and s- polarized light.

![Figure 1.12: Schematic of Ellipsometry set-up [Ref 95]](image)

Spectroscopic ellipsometry is a non-destructive and fast measurement technique. Advantages of this technique are high precision and thickness sensitivity (~ 0.1 Å). Determination of film thickness and optical constants is possible. Disadvantages are
requirement of optical model in data analysis and difficulty in characterization of low absorption coefficient (< 100 cm\(^{-1}\)). The spot size of beam is typically several millimeters, leading to low spatial resolution of measurement.

1.8.6 Scanning electron microscopy (SEM)

SEM is a non-destructive technique that reveals information regarding the morphology of the material. In this technique high energy electrons (30-40 keV) are incident on the sample. Interaction of electron beam with sample surface emits secondary electrons (~ 50 eV) that are detected by appropriate electronics and analyzed further. In conventional SEM instruments, electron beam is thermionically emitted from electron gun fitted with a filament. Filaments are generally made of tungsten or lanthanum hexaboride. The filament is heated by passing electric current through it. When heat generated is greater than the work function of the material, electrons are liberated. Thermionic sources have relatively low brightness; there can be evaporation of cathode material and thermal drift during operation.

The use of field emission scanning electron microscope (FESEM) which is advanced type of SEM can avoid these problems. The field emission gun is usually a tungsten filament fashioned in shape of sharp tip. The emission is achieved by placing the filament in a high electric field gradient. The sharp tip of the filament (~100 nm) helps in concentrating the electric field such that the work function of the material can be overcome and there is emission of electrons. In case of FESEM variable apertures are used to refine the beam, smaller objective aperture sizes will produce images with spatial resolution 3 to 6 times better than conventional SEM. High quality, low voltage images are obtained with minimal charging of the sample. This eliminates necessity of coating insulating samples with a conducting layer.
1.8.7 Energy dispersive X-ray analysis (EDAX)

EDAX is complementary to SEM. The qualitative / quantitative measurement of elemental composition present in the sample is obtained by EDAX. This technique operates on principle of detection of characteristic X-rays emitted by atoms of elements when electron beam interacts with the sample. The basic components of EDAX are X-ray detector, pulse processor (to measure voltage corresponding to X-ray energies) and a computer. The size of voltage pulse is proportional to energy of X-rays. Elemental distribution maps or elemental line profiles can be obtained by EDAX.

1.8.8 Scratch adhesion testing

The scratch adhesion testing is used to determine the cohesive and adhesive strength of the samples by measuring the critical loads at which failures occur in the sample. In this method, a diamond indenter is drawn on a coated surface under increasing load (either stepwise or continuous) until at particular load known as critical load \((L_c)\), where failure event occurs. If the failure event represents loss of coating-substrate adhesion then critical load is used as a qualitative measure to determine the coating substrate adhesion. However, in practice a range of failure modes can occur, some are dependent on adhesion, while others are dependent on plastic deformation and fracture within the coating. The study of these failure modes is important in assessing coating quality for tribological applications. The scratch track is studied with the help of reflected light microscopy and scanning electron microscopy.

1.8.9 Stylus Profilometer:

A stylus profilometer is an instrument used to measure the surface profile of thin films. Measurement of surface roughness and film thickness is done by using stylus
profilometer. A diamond stylus is moved along the surface of the film at a constant velocity for a specified distance and under a specified force. The curvature of the diamond tip is typically 10 µm. The film is masked during deposition stage so that a step is formed. The step height is measured by the pickup system and recorded as the thickness of the film. A typical profilometer can measure small vertical features ranging in height from 10 nm to 1 mm. The height position of the diamond stylus generates an analog signal which is converted into a digital signal stored, analyzed and displayed. The radius of diamond stylus ranges from 20 nm to 50 µm, and the horizontal resolution is controlled by the scan speed and data signal sampling rate. Smaller the tip radius of the stylus greater is the accuracy in the measurement.

1.8.10 X-ray absorption Spectroscopy (XAS):

When the incident X-ray energy matches the binding energy of the electron of atom within a sample, there is increase in absorption of X-ray. Here an absorption edge is observed due to drop in transmitted X-ray intensity. Each element has a set of unique absorption edges corresponding to different binding energy of electrons. The X-ray absorption spectrum is divided into two regions (Figure 1.13) namely, X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS).

XANES is the region including pre-edge and the absorption peak. It is strongly sensitive to formal oxidation state and coordination chemistry of absorbing atom. While EXAFS deals with the measurement of fine structures in the X-ray absorption spectra from 50 to 1000 eV above the absorption edge of the atoms in a material.
The interference of outgoing photoelectron with the scattered wave from surrounding atoms causes EXAFS (Figure 1.14). The regions of constructive and destructive interference are respectively seen as maxima and minima giving rise to oscillations in EXAFS. The fine
oscillatory structure in the X-ray absorption spectra of a particular species of atom gives precise information regarding the radial arrangement of atoms around that element, the number and nature of neighboring atoms. With the advent of modern bright synchrotron radiation sources, this technique has emerged out to be most powerful for local structure determination which can be applied to any type of material viz. amorphous, polycrystalline, polymers, surfaces and solutions [97]. As synchrotron sources are bright, concentration of absorbing element required for analysis can be in few ppm.

1.8.11 Thermo gravimetric analysis (TGA)

In TGA, the weight of the sample is recorded as a function of time as temperature is increased at a controlled uniform rate. Loss of water of crystallization or volatiles is revealed as weight loss. Oxidation or adsorption of gas shows up as weight gain. TGA instrument consist of a high precision balance with a furnace programmed for linear rise of temperature with time. Sample is then heated either in inert atmosphere or vacuum.

1.9 Scope of work/ thesis

Since plasma is a dynamic medium having immense potential applications, the interaction of plasma with surfaces becomes complex. Considering the various technological applications of yttria and yttria stabilized zirconia coatings, deposition of these coatings with plasma medium assumes significance. There are various process parameters of capacitively coupled RF plasma enhanced MOCVD such as the choice of substrates, the nature of precursors, deposition pressure, oxygen partial pressure, distance between the electrodes, substrate temperature, temperature at which the precursors are heated and the self bias. All of these parameters affect the properties of the deposited films. It then becomes important to
study the effect of these process parameters on the properties of deposited films to gain knowledge about the experimental conditions under which film with desired properties can be obtained. The correlation of some of these deposition parameters such as the self bias, precursors, temperature of precursors with the properties of the deposited films was done and understanding is sought on the role played by these key parameters in determining the physical and chemical properties of yttria and yttria stabilized zirconia thin films.

**Thesis organization**

The thesis is organized into seven chapters.

Chapter 1 gives a brief introduction about the oxides under study namely yttrium oxide and yttria stabilized zirconia. The chapter includes brief discussion on plasma, different types of plasma sources, application of plasma sources, various physical and chemical methods for thin film deposition. The different structures exhibited by Y$_2$O$_3$ and YSZ, their properties and applications are also discussed. A brief literature review on both the oxides is included along with description of working principles of different characterization techniques used.

Chapter 2 includes detailed experimental procedure for the deposition of Y$_2$O$_3$ and YSZ thin films by RF plasma enhanced MOCVD method. This chapter also includes short discussion on metalorganic precursors, mechanism of RF discharge and generation of RF self-bias voltage.

Chapter 3 gives details on deposition of Y$_2$O$_3$ thin films by RF plasma enhanced MOCVD method using Y(thd)$_3$ precursor. This chapter includes discussion on the effect of
variation of RF self-bias (applied to the substrates) on the properties of Y$_2$O$_3$ thin films studied by using different characterization techniques.

Chapter 4 includes discussion regarding EXAFS and AFM analysis of Y$_2$O$_3$ thin films deposited using Y(thd)$_3$ precursor under the varying influence of RF bias on the substrates. This chapter highlights the correlation of EXAFS data with the properties of Y$_2$O$_3$ thin films obtained by various characterization techniques.

Chapter 5 includes comparative study on Y$_2$O$_3$ thin films deposited by RF plasma enhanced MOCVD using two different metalorganic precursors, namely, Y(thd)$_3$ and Y(tod)$_3$. The structure and properties of the films are studied and compared using different characterization techniques.

Chapter 6 illustrates the deposition of yttria stabilized zirconia thin films by RF plasma enhanced MOCVD process using Zr(tod)$_4$ and Y(tod)$_3$ precursors. Discussion on effect of variation of yttria content on the deposited phases and properties of deposited thin films is given in this chapter.

Chapter 7 includes summary and highlights the important conclusions and findings of the investigations reported in this thesis.