

Chapter 2

Experimental Details

This chapter describes about the experimental details regarding the deposition of yttrium oxide (Y_2O_3) and yttria stabilized zirconia (YSZ) thin films by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) using metalorganic precursors. The chapter is divided into four sections. The first section describes the various metalorganic precursors that are used and their advantages. The second section gives details regarding the deposition system. Third section describes the significance of RF self-bias on the substrates during deposition. Deposition procedure for yttrium oxide and yttria stabilized zirconia coatings along with the cleaning procedure of the substrates is given in fourth section.

2.1 Metalorganic precursors

Generally, metalorganic precursors are compounds with a direct metal-carbon bond (σ or π). However precursors containing metal-oxygen, metal-nitrogen bond and even metal hydrides are also grouped under this category [99]. The decomposition of the precursor determines purity of the precursor and deposition rate of the films [99]. One of the major problems associated with metalorganic precursor is incorporation of carbon in the deposited film [100]. The way the precursor reacts can be modified by changing the ligands so that high purity, higher deposition rate can be obtained at lower temperature. Generally, it is observed that weak M-XC bond in precursor helps to reduce the amount of carbon incorporation in the deposited film. Intermolecular electrostatic forces tend to make the ionic molecules and polar molecules involatile. Larger the molecule, more it is polarizable, hence less is the volatility. However, larger ligands shield the metal centre and thus improve

volatility. So a compromise has to be achieved between effectively isolating the metal center and avoiding too large ligands [99].

Efforts are focused in the direction for developing suitable precursors for MOCVD satisfying the required properties. Precursors for MOCVD can be classified into four categories; metal alkoxides, metal alkylamide, metal alkyls and metal β -diketonates.

Alkoxides: These compounds have higher vapor pressure than β -diketonates but are less stable. This results in lowering of deposition temperature. They are more susceptible to water and oxygen. Oligomerization is a chemical process resulting into finite degree of polymerization of monomers. To inhibit oligomerization in metal alkoxides containing large, highly positively charged metal atoms, bulky ligands such as tert-butoxide must be used. This helps in preparation of volatile mononuclear alkoxide. However, these precursors contain unsaturated four-co-ordinate metal centers and tert-butoxide ligand undergoes a catalytic hydrolytic decomposition reaction in presence of trace water. These complexes therefore are air and moisture sensitive. This limits their shelf-life.

Alkylamides: These compounds have been found good for deposition of both metal nitride and metal oxide thin films. The carbon and nitrogen impurities were found to reduce by increasing the substrate temperature and flow rate of oxygen during deposition.

β -diketonate: These compounds are known for their volatility and thermal stability. Oligomerization can be controlled by steric bulk of ligands, manipulation of Lewis acid-base reactions by intramolecular donor sites or by additional ligands.

The β -diketonate precursors are used for the current work as they satisfy most of the required properties. They are easy for handling, non toxic, non corrosive and have high vapor pressure usually 1-10 torr in 100-300 °C temperature range [101]. In the present study,

(2,2,6,6-tetramethyl-3,5-heptanedionate) yttrium (commonly known as $Y(thd)_3$) and (2, 7, 7-trimethyl-3, 5-octanedionate) yttrium (known as $Y(tod)_3$) are used for deposition of Y_2O_3 while $Y(tod)_3$ and (2, 7, 7-trimethyl-3, 5-octanedionate) zirconia (known as $Zr(tod)_4$) are used for deposition of YSZ. The precursors were synthesized by ultrasound method. The details of precursor synthesis are given elsewhere [102, 103]. The thermo gravimetric analysis (TGA) on $Y(tod)_3$, $Y(thd)_3$ and $Zr(tod)_4$ precursors recorded at a pressure of 10^{-2} mbar is shown in **Figure 2.1(a)** , **2.1(b)** and **2.1(c)** respectively.

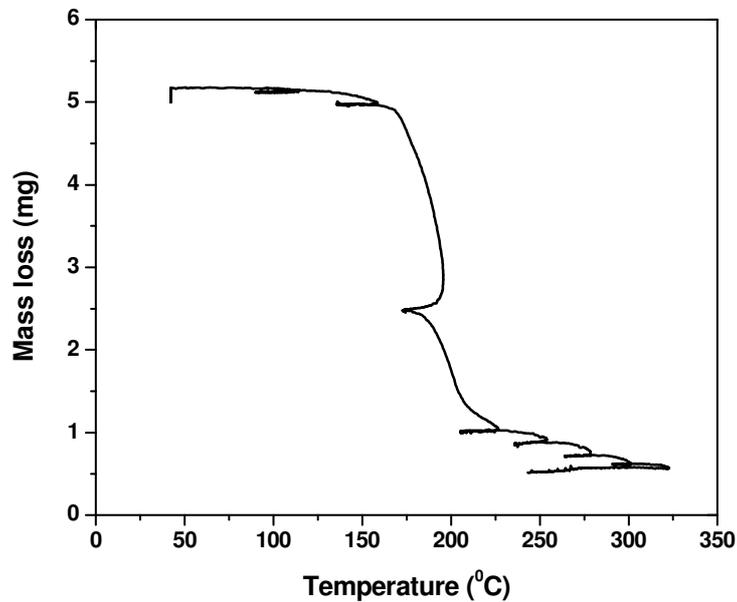


Figure 2.1(a): TGA plot of $Y(tod)_3$

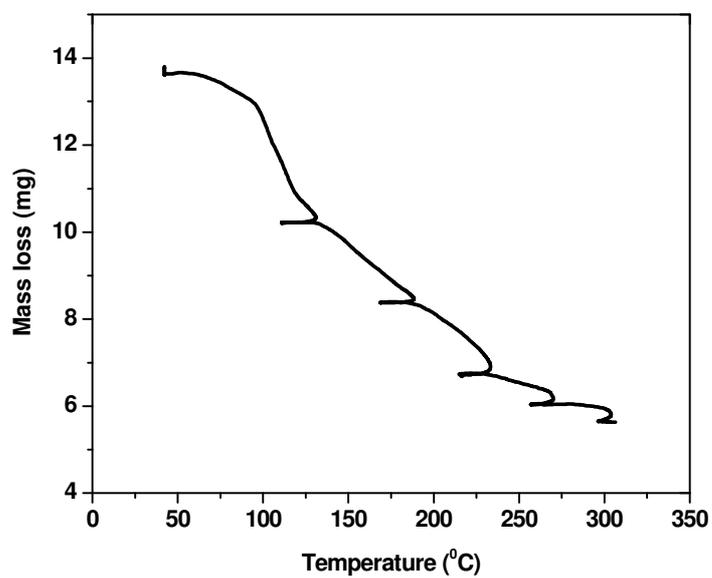


Figure 2.1(b): TGA plot of Y(thd)₃

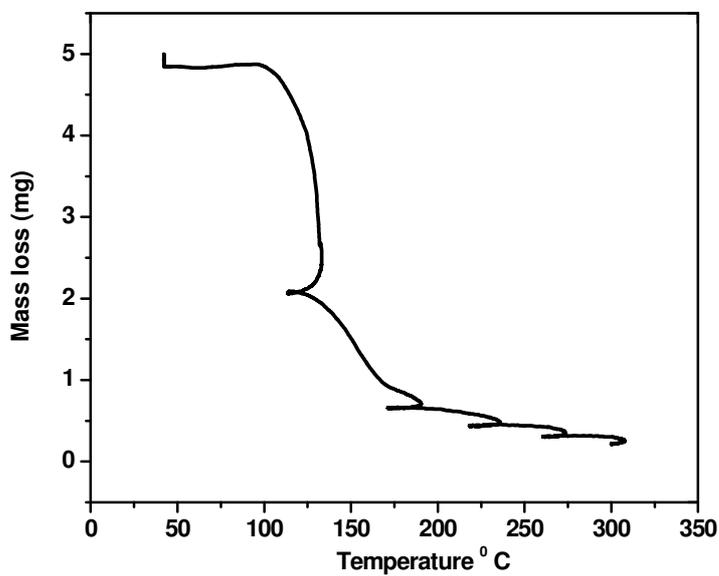


Figure 2.1(c): TGA plot of Zr(tod)₄

2.2 Deposition System

The schematic of the deposition system is shown in **Figure 2.2**.

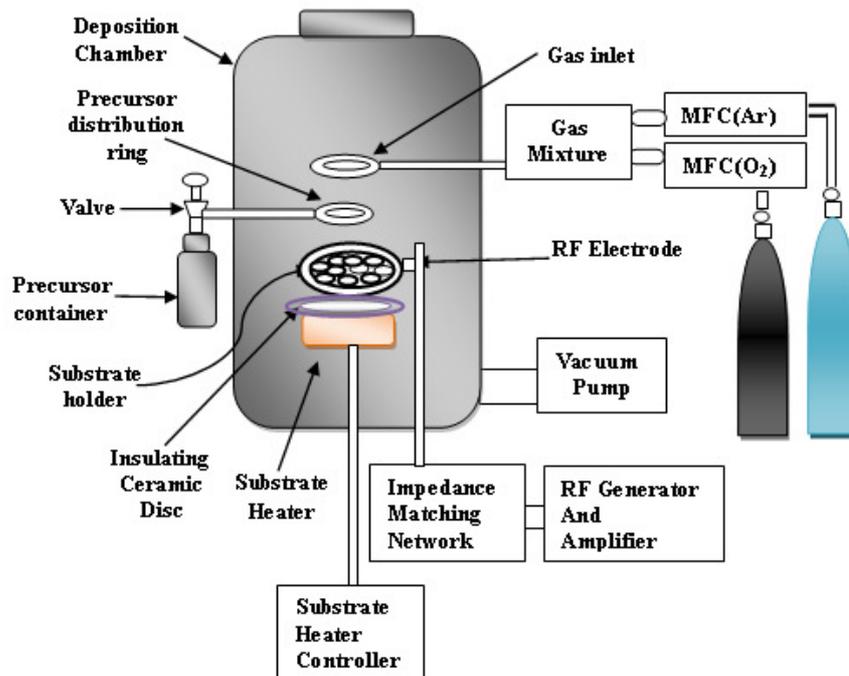


Figure 2.2: Schematic of deposition system for yttrium oxide thin films

The deposition is carried out in a cylindrical stainless steel chamber of 40 cm diameter and 50 cm height. The deposition chamber consists of a RF electrode and a substrate heater (capable of achieving a temperature of 700 °C) separated by a 3 mm thick ceramic ring. The ceramic ring acts as an isolator between the live RF electrode and grounded heater surface. The RF electrode is a S.S. plate with a concentric circular groove. This plate is fixed to a S.S. cylindrical rod; the other end of the rod terminates in a female type RF connector. The substrate holder is a circular S.S. disc with perforations in the form

of mesh that fits into the groove of the RF electrode plate. The electrode and the heater arrangement along with the ceramic ring can be moved in the vertical (Z) direction.

The precursor vapors are fed into the deposition chamber by a heated S.S. tube of 6.35 mm diameter. The precursor vapors are fed into the plasma as a shower by a S.S. ring that has perforations for uniform distribution of the precursor. Argon and oxygen gases are fed separately into the deposition chamber. The flow of these gases into the plasma chamber is controlled by mass flow controllers. The substrates are placed on the RF electrode. Distance between the substrates and the precursor distribution ring is kept as 4 cm during all depositions that are reported here. The precursor powder was pressed into pellets using a mechanical press. The precursor pellet is placed inside the S.S. container. The container is connected to precursor delivery line (S.S. tube) with a gate valve in between. The gate valve helps in controlling the flow of precursor vapors. The precursor delivery tube and precursor distribution ring are kept heated during the deposition to avoid condensation of the precursor in the delivery line. This helps in avoiding unnecessary blockage and ensures uniform flow of precursor vapor into the deposition chamber. The flow rate of the precursor vapors can be controlled by varying the temperature of the precursor container. The heating of substrates, precursor delivery tube and precursor distribution ring is achieved using a programmable heater controller.

RF signal generator (make-Rhode & Schrawz) along with a dual stage amplifier is used to apply power to the substrates through impedance matching network. Industrially allocated frequency of 13.56 MHz is used. The circuit diagram for the impedance matching network is shown in **Figure 2.3**. This circuit consists of a parallel capacitor (C_1) and a series inductor (L). A series capacitor (C_2) acts as a blocking capacitor. The LC circuit matches the

impedance of the chamber to the impedance of the RF generator (50 ohm). The blocking capacitor (C_2) stores charge and provides the DC self bias voltage. The self bias voltage is measured by an analog DC voltmeter (0-500 V). The capacitor and inductor values are determined with the help of Smith chart. Introduction to Smith chart and details regarding design of impedance matching network from Smith chart is given in Annexure I.

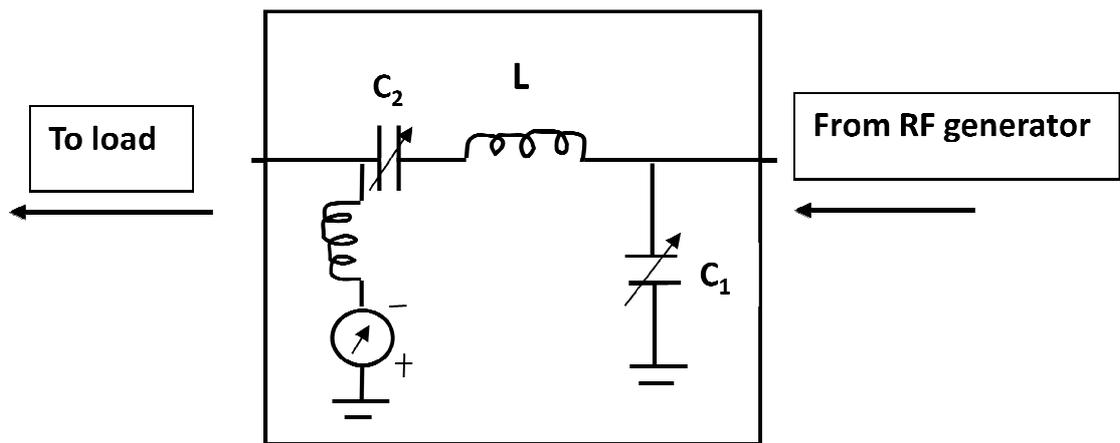


Figure 2.3: Impedance matching network

2.3 RF discharge

The process of RF discharge is collision dominated phenomena. In case of DC discharge, the electron can continuously gain energy, till it has sufficient energy to ionize the gas atom. However, in RF discharges the electrons can accelerate during half cycle and decelerate during the other half. Hence collisions play an important role, since after gaining maximum energy; the electron should transfer its energy to neutral atom. To achieve this condition, the pressure should be such that there should be probability of collision of neutral atom and electron, after electron has gained sufficient energy from the oscillating field. At low pressure, electron will keep on gaining and losing energy from the field, but the probability of collision will be less, as a consequence the breakdown field will increase. At

high pressures, the collisions will be frequent and electrons will not be able to gain sufficient energy from the field thereby leading to rise in the breakdown field strength. Therefore minimum field strength occurs at a condition where the collision frequency (ν_c) approximately equals the angular frequency (ω) of the oscillating field. The maximum amplitude of electrons (x) should be smaller than the chamber dimension (L) such that, $x \approx L/2$. Beyond this limit, the charged particles will hit the chamber walls and present a major source of loss to the system [5].

The RF self bias plays a very important role as a deposition parameter. It is generated basically due to the different response time of ions and electrons to the varying high frequency (13.56 MHz) AC field. During the positive half cycle electrons are attracted to electrode and the blocking capacitor (C_2) gets charged. During the consequent negative cycle, ions being sluggish cannot respond to the high frequency field and lag behind. Thus, in subsequent cycles, as the ions lag behind and due to high mobility of electrons, the blocking capacitor gets negatively charged and a self bias DC voltage is generated. The self bias dictates the energy of the impinging ions on the substrate and associated fragmentation of the precursors. The bias voltage involves both ion energy and ion flux. The energetic ions enhance surface migration and help in desorption of loosely bound species leading to uniform and dense film growth. The energy of bombarding ions thus decides the plasma chemistry and hence influences the properties of the deposited films. However high bias voltage levels can lead to resputtering or introduce distortions in the structure of films. The compressive stress developed is directly proportional to the bias value. The optimum bias voltage required will depend on the nature of material to be deposited and the type of application being focused on [104]. Depending on the dimensions of electrode and deposition

system, the power required to achieve a particular bias voltage will vary. For a given system, bias increases with power supplied and decreases with the pressure in the chamber.

2.4 Deposition Procedure of Y_2O_3 and YSZ thin films

The substrates used for deposition were silicon (100), quartz, stainless steel and tantalum. The average roughness values of uncoated substrates were 1.5 nm (silicon), 1.7 nm (quartz), 0.03 μm (stainless steel) and 0.05 μm (tantalum). Silicon wafer was cut with the help of diamond cutter into pieces of required dimension. The dimension of quartz and tantalum coupons was 1cm x 1 cm. Mirror polished 10 cm diameter steel discs were also used as substrates.

Silicon substrates were cleaned with standard RCA cleaning procedure. This procedure consists of following steps,

- i. Organic clean: The substrates were placed in solution of $H_2O:H_2O_2:NH_4OH$ in proportion of 5:1:1 and kept heated at 75 °C for 20 minute. Insoluble organic contaminants are removed. Then substrates are rinsed ultrasonically in de-ionized (DI) water for 15 minute.
- ii. Ionic clean: Then substrates are heated in a solution of $H_2O:H_2O_2:HCl$ in proportion of 6:1:1 at 75 °C for 20 minute. This removes ionic and heavy metal atomic contaminants. Then the substrates are rinsed ultrasonically in deionised water for 15 minute.
- iii. Finally, the silicon substrates are dipped in solution of $H_2O:HF$ in proportion of 50:1 for few seconds and then rinsed in deionised water for 15 minute.

The RCA procedure does not attack silicon and only a thin layer of silicon dioxide is removed.

The quartz, tantalum and stainless steel substrates were first washed with soap solution to remove traces of machining oil and then ultrasonically cleaned in de-ionized water. This was followed by ultrasonic rinse in methanol for 20 minutes. All the substrates were dried with help of IR lamp before transferring to the chamber.

After placing the cleaned substrates on the RF electrode, the chamber along with the precursor container and gas delivery lines were evacuated to a base pressure of 1×10^{-2} mbar using a rotary vacuum pump. The precursor container was then slowly heated to a desired temperature. The delivery lines and precursor distributor ring were also heated to avoid condensation of precursor in its path (this is necessary to achieve proper flow of precursor without any blockage in the delivery lines). The substrates were then heated to a temperature of 350 °C with the help of substrate heater. Prior to the deposition, the substrates were sputter cleaned using plasma of argon gas at a substrate bias of -125 V for 20 minutes. For deposition, plasma of argon (2 sccm), oxygen (10 sccm) and precursor vapors was used. Argon being a heavy atom assists in fragmentation of bulky precursors and bombarding of the growing film surface. The bombardment also helps in removal of loosely bonded species, resulting in film densification. Additional oxygen supply during deposition results in films with good stoichiometry and decrease in carbon incorporation [76]. All depositions were carried out for time duration of 60 minutes.

2.4.1 Deposition of Y₂O₃ coatings

Using the above procedure, yttrium oxide thin films were deposited. Two sets of studies were carried out regarding the deposition of Y₂O₃ coatings.

i) Effect of RF self bias on the properties of the Y_2O_3 thin films: To study the effect of RF self bias on the properties of the films, a series of six films were deposited by varying the self bias voltage on the substrates from -50 V to -175 V in steps of -25 V keeping all other experimental parameters same. The precursor used was, (2,2,6,6-tetramethyl-3,5-heptanedionate)yttrium known as $Y(thd)_3$. The actual experimental details and characterization of the deposited films are discussed in chapter 3.

ii) Comparison of heptanedionate and octanedionate precursors: Yttrium oxide thin films were deposited using two different metalorganic precursors, viz, $Y(thd)_3$ and $Y(tod)_3$ by process of RF plasma assisted CVD described above. The discussion on experimental deposition parameters and characterization of the thin films are discussed in chapter- 5.

2.4.2 Deposition of Ytria stabilized zirconia coatings

The schematic of the deposition system for deposition of YSZ thin films is shown in Figure.2.4.

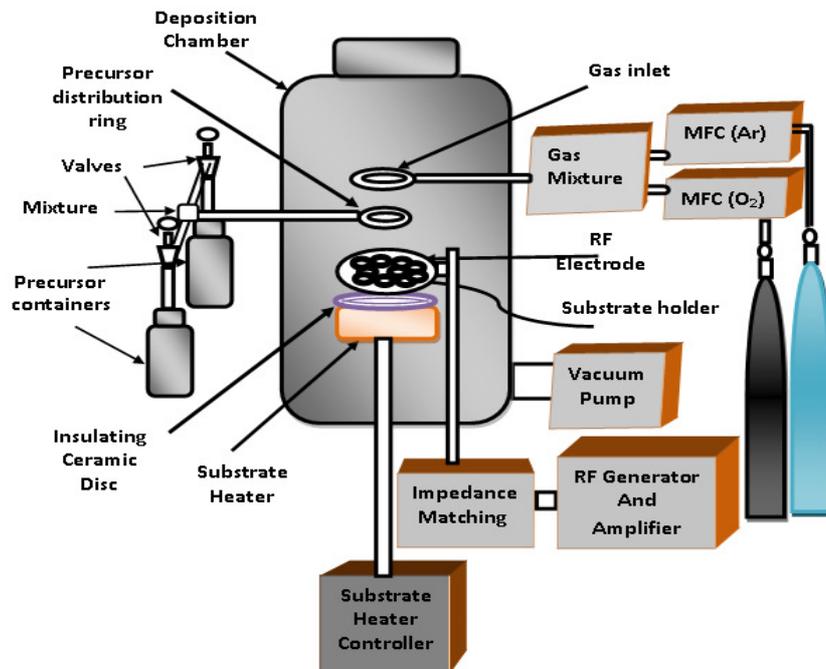


Figure 2.4: Schematic of deposition system for YSZ thin films

The deposition system for YSZ coatings is similar to that of the Y_2O_3 coatings except that there are two separate precursor containers. For deposition of YSZ coatings, (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. $Y(\text{tod})_3$ and $Zr(\text{tod})_4$ powders are placed in pellet form in two separate containers. The deposition procedure is similar to that of Y_2O_3 . Here $Zr(\text{tod})_4$ is kept at constant temperature of 220 °C and three different films are deposited by maintaining the temperature of $Y(\text{tod})_3$ containing precursor at three different temperatures; 110 °C, 130 °C and 160 °C to study the associated phase changes with variation of yttria content in the films. Three films were deposited by varying the yttria content in the films. The effect of variation of yttria content on the properties of zirconia is studied and details are discussed in chapter-6.