Chapter 7

Summary and Conclusions

The primary objective of the investigations reported in this thesis is to optimize the process parameters for deposition of yttrium oxide (Y_2O_3) and yttria stabilized zirconia (YSZ) coatings by the process of RF plasma enhanced metalorganic chemical vapor deposition, characterize the deposited coatings by various techniques and explain the characterization results in terms of variations in the deposition process parameters. RF effects can permeate through dielectrics hence deposition of dielectric (ceramic) coatings become feasible under the influence of RF bias on the substrates. By using RF plasma enhanced CVD, thin films can be deposited at low vacuum (rotary) level and hence minor fluctuations in the operating pressure does not create problems as regards to the stability of the plasma during deposition. The various process parameters, such as type of precursor, pressure, substrate temperature, RF self bias on electrode, etc affect the properties of the deposited films. Hence efforts are made to study the effect of variations of some of these process parameters on the properties of the deposited coatings.

The deposited Y_2O_3 and YSZ thin films are characterized by using various characterization techniques such as stylus profilometry, GIXRD, XPS, FTIR, spectroscopic ellipsometry, SEM, EDAX, EXAFS, XANES, AFM and tribological measurements.

There are very few reports on deposition of Y_2O_3 films using RF plasma enhanced MOCVD. To the best of my knowledge, the significant role played by RF self-bias on the substrates during deposition on the properties of the deposited coatings is not reported so far. Hence systematic investigations are made to study the effect of variation of RF self bias on the substrates during deposition (from -50 to -175 V) on the properties of deposited Y_2O_3 films using $Y(thd)_3$ precursor.

Self generated RF bias voltage determines the plasma chemistry and energy of impinging ions on the substrates, thus it is playing a very important role in determining the properties of deposited films. To get information on effect of RF bias variation on local structure of deposited Y_2O_3 thin films, the films are analyzed by EXAFS by probing absorption at Y K-edge. The changes in morphology are studied by AFM. The changes in bond length, co-ordination and disorder parameter obtained by EXAFS data analysis are correlated with the properties of deposited Y_2O_3 thin films.

Type of metalorganic precursor used and its decomposition characteristics, decides the deposition rate and amount of carbon incorporation in the film. This ultimately determines the structure and chemical composition of the deposited films. Hence a comparative study on Y_2O_3 films deposited using $Y(thd)_3$ and $Y(tod)_3$ precursor is done by studying the properties of films deposited by using these two precursors, keeping all other experimental parameters same.

In the present work, yttria is used to stabilize zirconia. Keeping all other experimental parameters same, three films are deposited by varying the concentration of yttria as 4, 5 and 9 mol percent. Depositions are done using $Y(tod)_3$ and $Zr(tod)_4$ precursors. To the best of my knowledge deposition and characterization of YSZ thin film using these octanedionate (tod) precursors is not reported so far.

7.1 Important Conclusions

From the investigations reported here it is evident that RF self bias plays a very important role in deciding about the properties of the deposited yttrium oxide films. Further, it is evident that deposition of Y_2O_3 films on silicon substrates is possible at a reasonably low substrate temperature of 350 °C using a RF plasma MOCVD process. Plasma medium allows uniform mixing of precursors resulting in uniform deposition. Due to deposition under the influence of highly energetic plasma constituents, the deposited coatings exhibit better optical properties without any post treatment. It is seen that all deposited films are transparent from deep UV to near IR range, a very important property that is useful in fabrication of protective optical layers. The results indicate that the reactivity of oxygen in plasma is sufficient and hence degree of non stoichiometry in the deposited films is less.

The films deposited under varying influence of RF self bias on the substrates show changes in the texture and properties of the films indicating a strong dependence of the properties on the substrate bias during deposition. The results of these investigations indicate that it is important to control the bias level on the substrates during deposition to get desired properties of the coating.

Local structure and surface morphology of Y_2O_3 thin films deposited by RF plasma-assisted MOCVD technique with different RF self-bias are investigated by EXAFS and AFM technique. As RF self-bias increases the Y-O bond length reduces and the deposited coating becomes more stoichiomeric and denser. However, for films deposited beyond a certain bias level, the Debye-Waller factor significantly increases manifesting realization of nanostructured films with structural distortion. AFM measurements also indicate that surface morphology of the films changes with change in bias voltage, where it is found that with initial increase in substrate bias more compact microstructure is realized with lower root minimum squared (r.m.s.) roughness. However, roughness increases significantly again as bias is increased beyond – 100 V possibly due to dominating effect of re-sputtering. The changes observed in local structural parameters of the films as obtained above could well be correlated with the observed macroscopic properties of the films.

Investigations reported here indicate that Y_2O_3 films deposited using $Y(thd)_3$ and $Y(tod)_3$ have BCC structure. Higher deposition rate can be achieved using $Y(tod)_3$ precursor. The film deposited using $Y(tod)_3$ precursor are nanocrystalline in nature. These films show enhanced refractive index indicating higher density of the film.

Dense and uniform yttria stabilized zirconia thin films are deposited by RF plasma enhanced MOCVD using octanedionate precursors, $Y(tod)_3$ and $Zr(tod)_4$. Deposition with RF plasma helps in enhancing the optical properties of the films. All films are found to be transparent from UV to near IR range and have nanocystalline structure. FTIR and XANES measurements confirm that the films with yttria content 4 mole % (film A), 5 mole % (film B) and 9 mole % (film C) are characterized by presence of predominant monoclinic, tetragonal and cubic phases respectively. AFM analysis suggest that as compared to films B and C, film A has least roughness value and tribological measurements confirm that the resistance to scratch induced crack and cohesive strength is also high in case of film A.

7.2 Scope of Future work

The RF plasma enhanced MOCVD technique holds a great promise for deposition of the thin films investigated here and also other films as it combines the advantages of CVD with bombardment of the growing film with energetic ions during deposition. By changing

RF self bias on the substrate during deposition, the coatings can be tailor-made according to the requirement. Variations in microstructure of deposited films from polycrystalline to nanocrystalline and amorphous is possible at low substrate temperature.

As deposited thin films exhibit good optical properties, they can be further investigated for its application in various areas like antireflection coatings and other optical coatings. PSZ coatings can be studied further for its use in tribological applications.

Systematic variation in process parameters for deposition of films using other precursors will also give a greater insight into the role played by precursors on the properties of the deposited films. Such studies can be carried out in future.

Studying the effect of varying RF self bias on the substrates during deposition on the properties of deposited partially stabilized zirconia and fully stabilized zirconia thin films will provide a window for deposition of the coatings with desired properties. Such investigations are extremely important for development of these coatings for various technological applications.