Plasma Assisted Metal Organic Chemical Vapour Deposition of Yttria and Yttria Stabilized Zirconia Coatings and their Characterization

Synopsis

Plasma as a medium has been proved to be very effective in deposition of thin films as well as for surface engineering and surface modification treatments [**1**]. Low pressure plasma assisted chemical vapor (CVD) deposition technique present significant advantages as compared to conventional CVD technique. Due to high internal energy of plasma medium, deposition can be done at lower substrate temperature. Further, there is uniform mixing of precursor vapors that results in uniform and dense coatings. Because of the presence of the energetic particles, the precursor fragmentation is effective that results in desired chemical reactions [**2**]. Radio frequency plasma enhanced CVD is one such technique. While RF power can be coupled to the plasma in an inductively coupled or capacitively coupled manner, here capacitively coupled RF plasma discharge at 13.56 MHz is used. These type of plasmas are characterized by plasma density of ~ 10^9 -10^{10} cm^{-3} and plasma potential of approximately 100 V. A 40 cm diameter stainless steel chamber is used for deposition. An impedance matching network is used to couple RF power to the electrode on which substrates are placed. Additional advantage of capacitively coupled RF plasma enhanced CVD process is that it is possible to self bias the substrate to a DC negative potential. Due to presence of negative self bias on the substrates and high plasma potential, the ions are accelerated towards the substrates leading to compact thin films.

In the present work capacitively coupled RF plasma has been used to deposit yttrium oxide (Y_2O_3) and yttria stabilized zirconia (YSZ) thin films by metalorganic chemical vapor deposition (MOCVD). β diketonate precursors, (2,2,6,6,tetramethyl-3,5-heptanedionate)

yttrium (known as $Y(thd)_3$) is used for deposition of yttrium oxide while (2,7,7-trimethyl-3,5-octanedionate) yttrium (known as $Y(tod)_3$) and (2, 7, 7-trimethyl-3, 5-octanedionate) zirconia (known as $Zr(tod)_4$) is used for deposition of yttria stabilized zirconia thin films. Plasma assisted MOCVD has emerged as one of the promising techniques for deposition of thin films. MOCVD technique has various advantages like low deposition temperature, good conformal coverage, uniform coating of the substrate, possibility of large scale production and ease of compositional control in complex films. Different types of thin film coatings of oxides, carbides, borides, nitrides, silicides and chalcogenides can be deposited by MOCVD [**3, 4**].

Yttrium oxide is a refractory ceramic with high melting point (2410 °C). It is used as a corrosion resistant coating [**5**]. It has high dielectric constant (~18) and good lattice matching with silicon, hence Y_2O_3 is considered as a potential candidate for use in microelectronic industry [**6**]. Y_2O_3 has wide band-gap (~5.1 eV) and is transparent from near infrared to ultraviolet region of electromagnetic spectrum hence it finds application as antireflection and protective coating [**7**].

Zirconium oxide (ZrO_2) is a wide band gap (~5.1eV) material with high dielectric constant (~18). It is chemically inert. Hence ZrO_2 thin films are finding applications as dielectric material in microelectronic industry [**8**]. It exists in monoclinic form at room temperature and undergoes destructive phase transition with temperature rendering it useless for technological applications. Doping ZrO_2 with divalent or trivalent dopants can stabilize high temperature phases at room temperature. Fully stabilized zirconia finds applications in oxygen sensor and as electrolyte in solid oxide fuel cells (SOFC). Partially stabilized zirconia

(PSZ) is known for its mechanical properties and hence used as wear and fracture resistant coating [**9**].

The above mentioned oxide systems were chosen during the studies reported here because of their stated potential applications. The objective of this thesis is to deposit these films by plasma assisted MOCVD process characterize the deposited coatings and correlate the observed properties with the process parameters.

The investigations carried during the course of this thesis are organized into seven chapters. **Chapter 1** consists of introduction to plasma assisted CVD and about the oxide systems that are studied here. Structures of different phases of yttria and yttria doped/stabilized zirconia are discussed in brief. Literature review on yttrium oxide and yttria stabilized zirconia coatings, including different deposition techniques used along with characterization and applications of these coatings are discussed here. A brief discussion regarding working principles of characterization techniques that are used is also included. The discussion is on characterization techniques such as stylus profilometer, spectroscopic ellipsometry, glancing incidence X-ray diffraction (GIXRD), fourier transform infrared (FTIR) spectroscopy, X-ray spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and extended X-ray absorption fine structure (EXAFS).

Chapter 2 discusses about the experimental details. This chapter gives details about precursor selection, deposition system and experimental procedure. The substrates used for deposition were silicon, stainless steel (s.s.), quartz and tantalum. The substrates were cleaned by chemical method and then sputtered by argon plasma for 20 minute before deposition. Plasma of metal organic precursor vapors along with argon and oxygen gases is

used for deposition. It is possible to control the flow of metal organic precursor vapors by controlling the temperature of the precursor.

Chapter 3 discusses about RF plasma enhanced MOCVD of yttrium oxide thin films. The films have been deposited by using plasma of $Y(thd)_3$ precursor vapors along with argon and oxygen gases. The $Y(thd)_3$ precursor temperature is maintained at 190 °C. The RF self bias is varied from -50 volt to -175 volt in steps of -25 volt and films (6 no.) are deposited keeping all other experimental parameters same. Depositions are carried for a period of one hour at a substrate temperature of 350 °C. The films were characterized by XRD, XPS, IR spectroscopy, spectroscopic ellipsometry, and SEM. The structural and optical properties of the films change with bias. The content of adsorbed moisture decreases for film deposited at -75 V as compared to film deposited at -50 V. However, beyond bias level of -125 volt, sputtering effects dominate and there is formation of nanocrystalline phase indicating degradation in crystallinity of the deposited films. The films deposited at -75 V and -125 V are oriented in (111) direction which is the preferred growth direction where surface energy is minimum. Refractive index of the film deposited at -150 V is highest due to nanocrystalline nature of the film. Films deposited at -75 V and -125 V are oriented along (111) direction and show similar value of refractive index. There is change of orientation for film deposited at -100 volt which is due to change in oxygen vacancy ordering. Change in orientation causes strain in the film resulting in decrease in thickness and refractive index of the film. The refractive index for film deposited at -175 V has decreased due to sputtering and further degradation of the crystal structure. The extinction coefficient for all the films is zero indicating that the films are transparent from near IR to UV range of the electromagnetic spectrum; a property useful in fabrication of antireflection and protective coating [**2**].

Chapter 4 gives details regarding the EXAFS analysis on the deposited Y_2O_3 films under different bias conditions. EXAFS measurements on these samples at Y K edge are carried out in fluorescence mode at the Scanning EXAFS Beamline (BL-9) at the INDUS-2 Synchrotron Source (2.5 GeV, 100 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. For measurements in the fluorescence mode, the sample is placed at 45^o to the incident X-ray beam and the flourosecnce signal (I_f) is detected using a Si drift detector placed at 90^o to the incident X-ray beam. An ionization chamber is used prior to the sample to measure the incident X ray flux (I_0) and the absorbance of the sample ($\mu = \frac{I_f}{I_0}$) is obtained as a function of energy by scanning the monochromator over the specified energy range. The absorption spectra of the samples at Y K edge are recorded in the energy range 16960- 17650 eV.

It is observed that co-ordination number is higher for film deposited at -50 volt and thereafter decreases and remains constant with bias on the substrate. The bond length in general decreases with bias indicating decrease in hydroxyl content in the films. Film deposited at -100 volt shows abrupt decrease in bond length due to generation of compressive stress. This stress can arise due to increase in number of dangling bonds as orientation of film has changed to (100). The disorder factor is similar for films deposited at bias voltages from -50 to -125 V and is highest for films deposited at bias level beyond -125 volt due to dominance of sputtering effect. This result also corroborates with AFM measurements which indicate increase in root mean square roughness and entropy at high bias levels.

Chapter 5 describes about deposition and characterization of Y_2O_3 films deposited using two different β diketonate precursors; $Y(thd)_3$ and $Y(tod)_3$. The films were deposited at

RF self bias voltage of -75 volt on the substrates with 200°C precursor temperature and 350 °C substrate temperature. All other deposition parameters being same, the properties of the two films are compared with the help of various characterization techniques. The films were characterized by GIXRD, FTIR, XPS, spectroscopic ellipsometry and SEM. The octanedionate precursors are known for high volatility and less carbon contamination in the deposited films [**4**]. Due to high volatility of $Y(tod)_3$ precursor; the deposition rate is enhanced for the film deposited using $Y(tod)_3$ leading to increase in nucleation density and formation of nanocrystalline structure. The refractive index is enhanced for film deposited using $Y(tod)_3$ precursor.

Chapter 6 discusses about the deposition and characterization of yttria stabilized zirconia thin films by RF plasma MOCVD using $Zr(tod)_4$ and $Y(tod)_3$ precursors at self bias of -100 volts. The substrate temperature is maintained at 350 °C. Precursor $Zr(tod)_4$ is maintained at 220 °C while the temperature of $Y(tod)_3$ temperature is varied at 110 °C, 130 °C and 160 °C leading to 4 mol %, 5 mol % and 9 mol % of yttrium oxide incorporation in the films respectively. With the variation of yttria content in the film there is a variation in the deposited phase and the properties of the deposited films. The deposited films were characterized by GIXRD, FTIR, XPS, spectroscopic ellipsometry, AFM, EDAX, EXAFS and SEM**.** To study the mechanical behaviour, scratch adhesion test and measurement of coefficient of friction is done. The GIXRD results could not indicate about the exact amount of phases formed. However, phase identification is possible with the help of IR spectroscopy. The film with 4 mol % Y_2O_3 is a mixture of monoclinic and tetragonal phases, film with 5 mol % Y_2O_3 has majority of tetragonal phase while film with 9 mol % Y_2O_3 has cubic phase. The values of refractive indices obtained for the films are in conformity with the values

reported in literature. The extinction coefficient is zero for all the three films for the investigated range from UV to near IR. Study of mechanical properties indicates that the film with 4 mol % yttria possess highest wear resistance. EXAFS analysis supports the above findings and gives an idea about the location of oxygen vacancy. Zr^{+4} ion is retaining its co-ordination while co-ordination of Y^{+3} ion has decreased to 6 indicating that oxygen vacancies are located near the Y^{+3} ion

Chapter 7 summarizes the important conclusions and findings of the present work. This chapter also discusses about the scope for the future work.

References:

1. J Reece Roth, '*Industrial Plasma Engineering, Vol- 2: Applications to Nonthermal Plasma Processing*', published by Institute of Physics Publishing (Bristol and Philadelphia).

2. S. S. Chopade, S. A. Barve, K. H. Thulasi Raman, N. Chand, M. N. Deo, A. Biswas, Sanjay Rai, G. S. Lodha, G. M. Rao, D. S. Patil, '*RF plasma MOCVD of Y_2O_3 thin films: Effect of RF self-bias on the substrates during deposition'*, Appl. Surf. Sci. 285P (2013) 524-531.

3. F. Maury, '*Recent Trends in the Selection of Metal-Organic Precursors for MOCVD process'*, J. Phys. IV, 5 (1995), C5-449-C5-463.

4. Serej V. Pasko, Liliane G. Hubert-Pfalzgraf, Adulfas Abrutis, Phillippe Richard, Ausrine Bartasyte and Vida Kazlauskiene, '*New sterically hindered Hf, Zr and Y β-diketonates as MOCVD precursors for oxide films'*, J. Mater. Chem. 14, (2004) 1245-1251.

5. W. J. Varhue, M. Massimo, J. M. Carrulli, V. Baranauskas, E. Adams, '*Deposition of Y_2O_3 by plasma enhanced organometallic chemical vapor deposition using an electron cyclotron resonance source'*, J. Vac. Sci. Technol. A 11 (1993) 1870-1874.

6. J. J. Araiza, M. A. Aguilar-Frutis, C. Falcony, '*Optical, electrical and structural characteristics of yttrium oxide films deposited on plasma etched silicon substrates'*, J. Vac. Sci. Technol. B 19(6) (2001) 2206-2211.

7. G. Alarcón-Flores, M. Aguilar-Frutis, M. García-Hipolito, J. Guzmán-Mendoza, M. A. Canseco, C. Falcony, '*Optical and structural characteristics of Y_2O_3 thin films synthesized from yttrium acetylacetonate'*, J. Mater. Sci. 43 (2008) 3582-3588.

8. Cheol Seong Hwang, Hyeong Joon Kim, '*Deposition and characterization of ZrO_2 thin films on silicon substrate by MOCVD'*, J. Mater. Res. 8 (6) (1993) 1361-1367.

9. D. Majumdar, D. Chatterjee, '*X-ray photoelectron spectroscopic studies on yttria, zirconia and yttria-stabilized zirconia'*, J. Appl. Phys. 70 (2) (1991) 988-992.

Monitoring / Doctoral Committee:

S. No.	Name	Designation	Signature	Date
1	Prof. K. Dasgupta	Chairman		12/8/14
2	Prof. D. S. Patil	Guide & Convener		12/8/14
3	Prof. Pushan Ayyub	Member		12/8/14
4	Prof. N. K. Sahoo	Member		12/8/14