RF plasma MOCVD of Y_2O_3 thin films: Effect of RF self-bias on the substrates during deposition

S.S. Chopade^a, S.A. Barve^a, K.H. Thulasi Raman^e, N. Chand^a, M.N. Deo^b, A. Biswas^c, Sanjay Rai^d, G.S. Lodha^d, G.M. Rao^e, D.S. Patil^{a,*}

^a Laser and Plasma Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

^b High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India

^c Applied Spectroscopy Division, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India

^d Indus Synchrotron Utilization Division, RRCAT, Indore 452013, India

^e Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Yttrium oxide (Y_2O_3) thin films have been deposited by radio frequency plasma assisted metal organic chemical vapor deposition (MOCVD) process using (2,2,6,6-tetramethyl-3,5-heptanedionate) yttrium (commonly known as Y(thd)₃) precursor in a plasma of argon and oxygen gases at a substrate temperature of 350 °C. The films have been deposited under influence of varying RF self-bias (–50 V to –175 V) on silicon, quartz, stainless steel and tantalum substrates. The deposited coatings are characterized by glancing angle X-ray diffraction (GIXRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry and scanning electron microscopy (SEM). GIXRD and FTIR results indicate deposition of Y_2O_3 (BCC structure) in all cases. However, XPS results indicate nonstoichiometric cubic phase deposition on the surface of deposited films. The degree of nonstoichiometry varies with bias during deposition. Ellipsometry results indicate that the refractive index for the deposited films is varying from 1.70 to 1.83 that is typical for Y_2O_3 . All films are transparent in the investigated wavelength range 300–1200 nm. SEM results indicate that the microstructure of the films is changing with applied bias. Results indicate that it is possible to deposit single phase cubic Y_2O_3 thin films at low substrate temperature by RF plasma MOCVD process. RF self-bias that decides about the energy of impinging ions on the substrates plays an important role in controlling the texture of deposited Y_2O_3 films on the substrates. Results indicate that to control the structure of films and its texture, it is important to control the bias on the substrate during deposition. The films deposited at high bias level show degradation in the crystallinity and reduction of thickness.

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1. Introduction

Because of its attractive properties, yttrium oxide (Y_2O_3) is an important material for various technological applications. It has unique properties such as high melting point (2410 °C) and is chemically inert and hence it can be used as corrosion resistant coating. It has high electrical resistivity (10^{11} – 10^{12} Ω cm), high-energy band gap (5.5 eV), high-dielectric constant (~ 13) and hence it is considered as an alternative to replace SiO_2 in microelectronics industry. Y_2O_3 is also transparent in ultraviolet and visible range of the electromagnetic spectrum and therefore it has important applications as antireflection and protective layer [1].

Due to the immense technological applications of Y_2O_3 , research and development on Y_2O_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_2O_3 have been deposited by spray pyrolysis [2], thermal oxidation [3], thermal CVD in atmospheric pressure [4], low pressure CVD [5], plasma assisted CVD [6], metal organic CVD [7], molecular beam epitaxy [8], atomic layer deposition [9], electron beam evaporation [10], ion beam assisted deposition [11], pulsed laser deposition [12,13] and radio frequency sputtering [14,15].

We have used radio frequency (RF) plasma assisted CVD for deposition of Y_2O_3 thin films. Advantages of plasma CVD over conventional CVD methods are that deposition is possible at low substrate temperature. The precursor molecules are fragmented in plasma, resulting in increased reactivity. There is also uniform mixing of various precursors resulting in deposition of uniform and non-porous coating. For this deposition process, the precursors should be in gaseous form or precursors with high vapor pressure at reasonably lower evaporation temperature can be used. Metal organic precursors like β -diketonates satisfy this condition and are

* Corresponding author. Tel.: +91 22 25595108; fax: +91 22 25505152.

E-mail addresses: dsptil@barc.gov.in, dinkarspatil@yahoo.com (D.S. Patil).

Fig. 1. Schematic of experimental setup for deposition of Y_2O_3 thin films.

non-hazardous, stable and safe for handling. These precursors have been used previously for deposition of yttrium oxide as well as other oxides [16–19]. Depositions were carried out under varying influence of RF self-bias on the substrates. The RF self-bias on the substrates decides about the energy of the ions that are impinging on the substrates. This eventually decides precursor decomposition characteristics and the properties of the deposited films. Though deposition and characterization of Y_2O_3 thin films by different techniques have been reported by various investigators, to the best of our knowledge the deposition of these films using RF plasma and under varying influence of RF self-bias on the substrates during deposition is not reported so far. The objective of the investigations reported here is to deposit Y_2O_3 thin films under varying influence of RF self-bias on the substrates during deposition and study its effect on the properties of the deposited films. To investigate the role of RF self-bias on the substrates during deposition, the deposited coatings were characterized by various characterization techniques like: X-ray photoelectron spectroscopy (XPS), glancing angle X-ray diffraction (GIXRD), infrared (IR) spectroscopy, spectroscopic ellipsometry and field emission scanning electron microscope (FESEM).

2. Experimental

The schematic of RF plasma MOCVD deposition system is as shown in Fig. 1. Yttrium oxide thin films were deposited at different RF self-bias levels on the substrates during deposition, namely, -50 V (film A), -75 V (film B), -100 V (film C), -125 V (film D), -150 V (film E) and -175 V (film F). Precursor vapors of $\text{Y}(\text{thd})_3$ (2,2,6,6-tetramethyl-3,5-heptanedionate) yttrium along with oxygen and argon gases were used for deposition. The details of $\text{Y}(\text{thd})_3$ precursor synthesis are given elsewhere [20]. Silicon (100), stainless steel (S.S.), quartz and tantalum substrates were used for deposition. The average roughnesses of uncoated substrates were 1.5 nm (silicon), 1.7 nm (quartz), 0.03 μm (stainless steel) and 0.05 μm (tantalum). Silicon substrates were first cleaned using RCA procedure and then treated with 4% HF solution for 45 s to remove the native oxide layer on the substrate surface just before the deposition. Quartz, tantalum and stainless steel substrates were first cleaned with soap solution followed by ultrasonic cleaning in de-ionized water and then in methanol. The deposition chamber consists of a RF electrode and a substrate heater separated by a 3 mm thick ceramic ring that 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. The substrate holder is a circular S.S. disc with perforations in the form of mesh that fits into this groove of the RF electrode. The electrode and the heater arrangement along with the ceramic ring can be moved in the vertical (Z) direction. The precursor vapors are brought into the deposition chamber by a heated S.S. tube of 6.35 mm diameter. These 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 $\text{Y}(\text{thd})_3$ precursor in the form of 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 to control the flow of precursor vapors. The flow of the precursor vapors can be controlled by varying the temperature of the precursor container. However, during all depositions reported here the temperature of the precursor container is kept at 190°C . RF (13.56 MHz) power is applied to the substrates through impedance matching network.

After placing the cleaned substrates on the RF electrode, the chamber along with the precursor container and gas delivery lines are evacuated to a base pressure of 1×10^{-2} mbar pressure using a rotary vacuum pump. The precursor container is then slowly heated to a temperature of 190°C . The delivery lines (170°C) and precursor distributor ring (190°C) are 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 are then heated to a temperature of 350°C with the help of substrate heater. Prior to starting the deposition, the substrates are sputtered cleaned using plasma of argon gas at a substrate bias of -125 V for 20 min. For deposition, plasma of argon (2 sccm), oxygen (10 sccm) and $\text{Y}(\text{thd})_3$ vapors is used. Depositions are carried out by varying the substrate bias (-50 V to -175 V in steps of -25 V) levels by keeping all other parameters constant. All depositions were carried out for time duration of 60 min. The final operating pressure was $\sim 2 \times 10^{-2}$ mbar.

3. Characterization

The deposited films were characterized by GIXRD, XPS, FTIR, spectroscopic ellipsometry and FESEM. GIXRD was carried out using a $\text{CuK}\alpha$ radiation source using Bruker D8 Discover model. The incident (glancing) angle was fixed at 1.8° . The scans were taken in 2θ range of 10° – 90° with scan step of 0.02° per 3 s. XPS was done with SPECS GmbH spectrometer with Phoibos 100 MCD energy analyzer. The scans were taken with $\text{Al K}\alpha$ (1486.6 eV energy) with a pass energy of 22 eV. Microstructure was studied by using Carl Zeiss make FESEM Model No. ULTRA 55. Infrared spectra were recorded with Bruker Vertex 80V FTIR spectrometer configured with Mylar beam splitter and DTGS detector in Far-IR region at 4 cm^{-1} spectral resolution. A 11° reflection accessory was used for the measurements. Ellipsometric studies were carried out with a phase modulated spectroscopic ellipsometry unit (model UVSELTM 460 ISA JOBIN-YVON, SPEX) in the range 300–1200 nm. Thickness measurement was done using Dektak stylus profilometer. (model 150 Veeco).

4. Results

Results of thickness measurement are given in Table 1. It can be seen that film thickness varies with substrate bias during deposition and is maximum for film B.

Table 1
Thickness measurement results on deposited films at various RF self-bias voltages.

Film	Bias (V)	Thickness (nm)
A	–50	140
B	–75	250
C	–100	65
D	–125	200
E	–150	108
F	–175	75

4.1. Spectroscopic ellipsometry

Fig. 2 shows the variation of the refractive index with wavelength for the films that are deposited at different bias levels. All films show a fairly constant refractive index in the wavelength region of 600–1200 nm. As wavelength decreases below 600 nm, refractive index increases monotonically as reported in the literature [13]. There is a change of refractive index of the deposited films with bias. Film E shows the highest refractive index followed by films B, D, A, C and F. However, for all films extinction coefficient is zero in the investigated wavelength range (300–1200 nm), indicating that all films are transparent in this wavelength range.

4.2. Glancing angle X-ray diffraction

The GIXRD patterns taken on the films are shown in Fig. 3. From the X-ray diffraction patterns, it can be seen that the films A, B, C and D show deposition of Y_2O_3 with BCC structure. The diffraction lines corresponding to (2 2 2), (4 0 0), (4 4 0), and (6 2 2) reflections as indicated in JCPDF Card No. 79-1716 do match well with the observed pattern. Films E and F that are deposited at higher bias level on the substrate show no preferred orientation and indicate that they are losing crystalline nature with the increase in the bias level (i.e. with the increase in the energy of the ions that are arriving at the substrates). Film A shows growth along both (1 1 1) and (1 0 0) directions. While films B and D show texturized growth along (1 1 1) direction, film C shows texturized growth along (1 0 0) direction.

4.3. X-ray photoelectron spectroscopy

The XPS scans were taken with pass energy of 22 eV. Peaks corresponding to Y 3d and O 1s are scanned in detail with 0.1 eV scan step.

Fig. 2. Variation of refractive index for films deposited at different RF self-bias voltages.

Table 2
Semi-quantitative analysis (by XPS) of film surfaces from Y 3d peak.

Film	% Y_2O_3 content	% Y_2O_{3-x} content	% Y–OH/Y–OC content
A	57.15	10.9	31.8
B	70.29	10.6	19
C	77.8	4.10	18.06
D	73.37	10.6	16.03
E	61.02	18.8	20.16
F	69.89	8.33	21.77

These peaks are deconvoluted by using XPS Peak fit 4.1 program. The binding energy shifts were corrected using binding energy of physisorbed carbon at 284.6 eV as reference [21].

Y 3d deconvoluted peaks for films deposited at different RF self-bias voltages are shown in Fig. 4. The Y 3d core level is getting splitted into doublet ($Y 3d_{5/2}$ and $Y 3d_{3/2}$) due to spin orbit coupling. The doublet has energy separation of 2.1 eV and Y $3d_{5/2}$ to Y $3d_{3/2}$ areal intensity ratio is 1.5 [22]. The Y 3d peak is deconvoluted with Gaussian:Lorentzian (G:L) ratio of 5 with FWHM of individual peaks in the range of 1–1.8 eV and chi-square (χ^2) in the range of 1–2. Three different chemical environments are found for the yttrium atoms in all films. Peak pair with binding energy at ~156.8 eV and ~158.8 eV correspond to stoichiometric yttrium oxide, peak pairs with binding energy at ~157.8 eV and ~160 eV could be either Y–OH or Y–OC bonds. Y–OC will shift the Y 3d doublet to higher binding energy due to higher electro negativity of carbon [23]. Peak pairs with lower binding energy ~155.8 eV and ~158 eV indicate the presence of non-stoichiometry on the surface of deposited films [16]. The extent of nonstoichiometry of the deposited phase on the surface varies from 4% to 18% with bias as shown in Table 2.

Deconvoluted O 1s peaks for the films deposited at different RF self-bias voltages are shown in Fig. 5. The O 1s peak is deconvoluted with Gaussian:Lorentzian (G:L) ratio of 15 with FWHM of individual peaks in the range of 1–1.8 eV and chi-square (χ^2) value in the range of 1–2. The O 1s peak is deconvoluted into four sub peaks with binding energy 529 eV, 530 eV, 531 eV and 532 eV. Peak with binding energy of 529 eV corresponds to stoichiometric yttrium oxide, presence of peak with binding energy 530 eV indicates that there is non stoichiometry on the surface of deposited phase, peaks with binding energies 531 and 532 eV correspond to the presence of O=C=O and C=O bonds on the surface of deposited films. For film E, peak corresponding to binding energy of 528.5 eV correspond to Y–OH bond [24]. As Y_2O_3 is hygroscopic in nature, it absorbs moisture from the atmosphere and reacts to form hydroxide and carbonates. Since in situ sputtering of the sample surfaces prior to XPS scan is not done (to avoid modification of thin film surface) it can be seen that along with Y_2O_3 there is the presence of yttrium carbonate in all films [16]. Since moisture and carbon species are adsorbed on the surface of the film, quantitative analysis based on XPS from O 1s peak may not represent the actual bulk composition of films. Hence, semi-quantitative analysis is done only by taking into consideration Y 3d peak [25].

Semi-quantitative analysis from Y 3d peak indicate that the degree of stoichiometry of deposited phase on the surface of films is gradually increasing with bias (Table 2). However at bias levels beyond –100 V there is a decrease in degree of stoichiometry of deposited phase on the surface of films.

4.4. Field emission scanning electron microscopy

The surface microstructures of the deposited films along with the transverse cross-sections for films A–F as seen by SEM are given in Fig. 6(a–f). It is seen that the microstructure of the films is changing with the applied bias.

Fig. 3. X-ray diffraction pattern for films deposited at different RF self-bias voltages.

Fig. 4. Y 3d detailed XPS scans for films deposited at different RF self-bias voltages.

Fig. 5. O 1s detailed XPS scans for films deposited at different RF self-bias voltages.

4.5. Infrared spectroscopy

The Far-IR reflectance spectra taken on the films are shown in Fig. 7. The triplet consisting of peaks at 305 cm^{-1} , 330 cm^{-1} and 375 cm^{-1} confirm the presence of cubic yttrium oxide [26]. Additional peaks for cubic yttrium oxide are seen at $\sim 185\text{ cm}^{-1}$, 243 cm^{-1} , 350 cm^{-1} , 383 cm^{-1} , 395 cm^{-1} , 420 cm^{-1} , 435 cm^{-1} , 445 cm^{-1} , and 468 cm^{-1} [27–29]. The triplet is intense for films B and D as compared to other films. As information from IR peaks represent a bulk phenomena the intensity of IR peaks will be directly proportional to the thickness of the film.

5. Discussions

From the X-ray diffraction patterns, it can be seen that films A, B, C and D have polycrystalline BCC structure and there is a loss of crystalline nature in case of films E and F. Film A shows textured growth along both (1 1 1) and (1 0 0) directions. Films B and D show textured growth along (1 1 1) direction while film C show preferred growth along (1 0 0) direction. In case of films E and F there is a loss of crystalline nature of the films as is evident from the diffraction patterns that show two broad peaks centered at $2\theta = 29^\circ$ and 56° . The orientation of the films depends on the deposition method, temperature of the substrate, oxygen partial pressure and the total gas pressure during the deposition [22]. The interfacial reactions and the thickness of the interface also play a prominent role in deciding about the orientation as reported earlier by Cho et al. [30]. In the present case the substrate temperature, oxygen partial pressure and total gas pressure are kept same during all depositions. The initial pre-deposition treatment conditions are also same for all depositions. Therefore, the change in texture of the deposited films can be attributed to the variation in the RF self-bias level on the substrate during deposition. The net input power to the plasma will vary with the bias on the substrates. This power level decides about the fragmentation of the precursor and energy of the ions that are impinging on the substrates. This is also evident from the observed deposition rate variation with the bias.

At -50 V bias (film A) on the substrate, the net power fed in the plasma is relatively less as compared to the one at higher bias

levels. This affects the degree of ionization in the plasma. It is therefore clear that deposition rate is lower for the film A. Yttrium oxide has a bixbyite structure with ordered oxygen vacancies. The unoccupied oxygen sites form parallel strings along the four (1 1 1) directions of the unit cell. These strings help in migration of oxygen through the material as deposition proceeds. Therefore, (1 1 1) plane is the lowest surface energy plane of the bixbyite structure [31]. There is also a good lattice constant matching between Si (1 0 0) and Y_2O_3 (1 1 1) resulting in less defects during deposition [13]. Also in case of film deposited at -75 V (film B), there is enhanced degree of ionization of the plasma constituents and hence due to these reasons, film B has higher deposition rate as compared to the film A. It is seen that the thickness of film C is reduced drastically. This may be due to orientation of the film along (1 0 0) direction. Since (1 1 1) is the minimum surface energy plane, growth along (1 0 0) direction may produce strain in the film hampering the deposition rate. Film D that is oriented along (1 1 1) also shows enhanced deposition rate as compared to film C for the reasons mentioned.

Argon that is used during deposition produces heavy ions that can transfer momentum to the constituents of the plasma resulting in effective ionization of gases including precursor that is used for deposition [32]. However, as observed, at high bias level, use of argon gives undesirable effects as it can bombard the growing film surface with high energy and re-sputter the film. Hence as the bias level on the substrates increases further, the resputtering of the deposited surface by energetic ions that are arriving at the substrate surface is dominating, resulting in lower deposition rate as is observed in case of films E and F [33,34].

The optical constants of Y_2O_3 film are highly dependent on its microstructure [35] and even small changes in refractive index values may indicate significant changes in the microstructure of deposited films [36]. GIXRD pattern for film E shows broader peaks indicating reduction in grain size due to bombardment by energetic ions; also film E exhibits maximum refractive index. The enhanced refractive index may be due to formation of dense nanocrystals. This dense network of nanocrystals enhances the packing density as reported by Ramana et al. [35]. Packing density is higher for (1 1 1) plane [24] as compared to other planes hence films B and D that are textured along (1 1 1) direction show high refractive index. Film A

Fig. 6. (a–f) SEM images showing surface microstructures and cross-sectional views of the deposited films.

does not show any preferred orientation and hence has an intermediate value of refractive index. Orientation of film C is along (100) direction which is not densely packed as compared to (111) plane and hence it shows lower refractive index as compared to film B. A similar trend was also observed by Kim et al. [36]. Film F exhibits minimum value of refractive index this may be the result of further degradation in crystallinity of the film due to heavy bombardment of highly energetic ions [36].

The extinction coefficient of all films is zero from deep UV to near IR indicating that all the films are transparent within the region of

electromagnetic spectrum that is investigated here. All films are having a good band structure so there is no light absorption [13]. This also indicates that there is sufficient amount of oxygen ion activity during deposition. The energetic oxygen ions in the plasma can easily react with yttrium to form yttrium oxide films with maximum transmittance [11]. The observed transmittance properties and high refractive index of Y_2O_3 is very useful in developing antireflection and protective optical layers [22,35].

XPS being a surface sensitive technique it probes few layers on the surface of the films. GIXRD and IR results indicate deposition

Fig. 7. Far-IR reflectance spectra of Y_2O_3 thin films deposited at different RF self-bias voltages.

of single phase cubic structure; while XPS analysis indicates that the degree of stoichiometry of the deposited phase on the surface of the films varies with bias. The nonstoichiometry may be due to the presence of oxygen vacancies on the surface of the films. GIXRD and IR are bulk techniques, while XPS is a surface sensitive technique. GIXRD indicates deposition of single phase BCC structure for all the deposited films. IR peaks for reduced yttria at 170, 233, 407 and 431 cm^{-1} [25] are not seen for all the films indicating that the nonstoichiometric nature of films as seen by XPS analysis is only a surface phenomena, the bulk being polycrystalline BCC structure. As stated earlier, semi-quantitative analysis is done here by considering only Y 3d peak. As seen from Table 2, the XPS analysis indicates that the degree of stoichiometry is changing with bias. The degree of stoichiometry is bias dependent, increases with bias becomes maximum for film C and again decreases as bias is increased. At -50 V bias, the power fed in plasma is less and hence associated degree of ionization is less resulting in lower degree of stoichiometry as compared to films deposited at higher bias voltages. Further at this bias level, the bombarding ions have less energy and hence there can be formation of voids in the film. Formation of voids can lead to increased moisture absorption and subsequent formation of carbonate and hydroxide bonds on the film surface [37]. However, this being a surface phenomena, GIXRD pattern for film A indicates single phase BCC deposition. With the increase in the bias level, XPS analysis shows that degree of stoichiometry is also increasing as degree of ionization and energy of bombarding ions increase with bias. At bias voltages beyond -100 V , degree of stoichiometry of Y_2O_3 is decreasing. There is increase (4–5%) in the amount of yttrium carbonate for films E and F. This may be due to their nanocrystalline nature as nanoparticles have large surface area which favors the adsorption of atmospheric gases [38].

From FESEM results it is clear that the microstructure of the films is changing with bias. It can be seen that all films are dense and the grain size is changing with bias. For film A, grain size is approximately 25 nm. For film B, dense granular structure is visible

with grain size in the range of $\sim 40\text{--}50\text{ nm}$. For film D the grains have grown in elongated shape with grain size of $\sim 50\text{--}60\text{ nm}$. Films E and F are showing a broad XRD pattern indicating nanocrystalline structure formation. However, because of the fact that Y_2O_3 is highly hygroscopic, there is an enhanced tendency to pick up moisture at the grain boundary and this result in the degradation of the surface microstructure. Although granular structure is observed, the microstructural features are not clearly seen in case of films E and F. The cross-section images taken on freshly prepared fractured surfaces of all films indicate the deposition of dense films.

The Far-IR spectra show variation in intensity of the peaks with substrate bias. It is seen that the intensity of IR peaks is directly proportional to the thickness of the films. Sharp and intense triplet is obtained for films A–D. In case of films E and F the triplet at 302 cm^{-1} , 330 cm^{-1} and 375 cm^{-1} is relatively broader and shifted indicating degradation in crystalline nature [6]. Peak at 395 cm^{-1} is also present for all films and 468 cm^{-1} peak is present in spectra of films A–E. Peak at 243 cm^{-1} is observed for films A–C. 350 cm^{-1} and 418 cm^{-1} peaks are present for films A–C and E, F. Additional peaks at 183 cm^{-1} , 383 cm^{-1} and 435 cm^{-1} are observed for film E. Peak at 445 cm^{-1} is present for film F. Peaks beyond 300 cm^{-1} are due to deformation in YO_6 octahedra and motion of oxygen atoms and peaks below 300 cm^{-1} are due to motion of yttrium atoms in their octahedral [27]. These additional IR absorption peaks besides the triplet indicate the presence of cubic yttrium oxide phase in the films [27–29]. Thus, from IR analysis it is evident that though GIXRD pattern of films E and F are broad and diffused, these films show distinct peaks for Y–O bonding and hence are not completely amorphous.

6. Conclusion

From the investigations reported here 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. 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. It is seen that all films are transparent from deep UV to near IR range, a very important property that is useful in fabrication of protective optical layers. Different characterization techniques confirm deposition of single phase cubic Y_2O_3 on the substrates. 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.

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