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Growth and characterization of Sm_2O_3 thin films by spin coating technique

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Abstract : Samarium oxide (Sm_2O_3) thin films were deposited on glass substrate by using spin coating technique. These films were characterized for their structural, functional, optical and luminescent properties by means of XRD, micro Raman, UV, FTIR and Photoluminescence respectively. Optical absorption coefficient α(λ) had been evaluated in the inter band transition energy region and the obtained energy gap in between 3.15eV to 3.48eV. The XRD patterns of deposited thin films exhibited an amorphous nature at low temperature and transferred the polycrystalline stated at above 550° C. Raman active modes of spin coated thin films revealed obviously B-type of Sm_2O_3. The FTIR analysis confirmed the presence of Sm-O stretching vibrations (ν-Sm-O) in all the samples. The coated Sm_2O_3 thin films are transparent at low energy of visible region and an excellent absorbency at higher energy of UV region. The Photoluminescence (PL) spectra of Sm_2O_3 have exhibited both blue and visible emissions.
Keywords: Sesquioxide, Rare earth compounds, spin coating, thin film.

Introduction:

In thin film science and technology, Rare Earth metal Oxides (REO) have been intensively studied for numerous application such as microcircuit elements, photoelectric devices, MIS structures, electrical switches, reprogrammable memory elements and optical devices. Rare earth oxides are examples of such materials, which are characterized by high values of dielectric constant, high resistivity chemical and thermal stability[1,2]. Samarium oxide is a rare earth oxide (REO) belonging to the lanthanide (III) series. It is an attractive REO material to achieve the comparable dielectric properties as La_2O_3. Sm_2O_3 thin films had been prepared and reported by various techniques like Physical Vapor Deposition (PVD)[3-9], Chemical Vapor Deposition (CVD)[10-13] and hydro-thermal method whereas sol-gel spin coating method is in meager hence in the present study sol-gel spin coating has been chosen to prepare Sm_2O_3 film. The prepared thin films are subjected to be investigated on structural, optical, Raman shift, functional group and luminescent properties of Samarium oxide thin films.

Experimental

Samarium oxide (Sm_2O_3) thin films were synthesized by spin coating technique using samarium acetate hydrate $(CH_3CO_2)Sm.H_2O$ as the starting materials. At first 0.01M of Samarium acetate was added in the 5ml of distilled water and allowed to mix through the magnetic stirrer to obtain homogeneous mixture. Prior to deposition, the glass substrates were cleaned with chromic acid, ethanol, detergent, deionized water and acetone. Consequently as for the sol-gel process, 0.02M of Poly Vinyl Pyrrolidone (PVP) was added into the above solution as coating additive. The mixed solution was stirred vigorously at 60° C for 30 mins. The filtered solution was deposited onto a glass substrate by a single wafer spin processor. After setting the substrate on the substrate holder onto the spin coaters, the coating solutions was dropped and spins casted at different rpm such as 2000, 2500 and 3500. The obtained thin films were annealed at 550°C and 600°C.

Results and Discussion

X-ray Diffraction Analysis

The XRD pattern of different rpm and various annealed temperature of the spin coated Sm_2O_3 thin films is shown in Fig 1. The film coated at room temperature is not shown in figure, because it is being in amorphous form.

When the obtained film coated at 2000 rpm and annealed at 550° C exhibits, the planes 202 and 220 at 2θ=22° and 24° respectively. These emerging planes are due to Sm_2O_3 which is an indication of crystallization of Sm_2O_3, which is an indication of crystallization of Sm_2O_3 from amorphous [14, 15]. As rpm increases at 2500 the intensity of the plane 220 remain same whereas the reflection at 202 has attained diminutive in intensity. This tendency of change in reflections reveals that, the textured growth of Sm_2O_3 cubic crystallization on the substrate.

Few new reflections at (200), (111), (310) plane were noticed when the film coated at 3500 rpm and annealed at 550° C. The persistent reflection at 220 and 202 had vanished consecutively. The noticed new reflections state to us the formation of Sm_2O_3 had cubic poly crystallization on substrate surface. According to Gin-YaAdochiet.al., and Baker et. al., the formation of cubic structured Sm_2O_3 is B-type rare earth sesquioxides in behavior [16, 17]. This type of Sm-oxide is stable at low temperature and at ordinary pressures [18].

The Sm_2O_3 thin films coated at various rpm and annealed at 600° C is shown in fig.1 (d,e). As temperature increases all the diffraction reflections had been disappeared and the reflection (202) is only appeared. This shows that the conversion of cubic crystalline of Sm_2O_3 into monoclinic Sm_2O_3 crystalline structure [12]. The formation of the monoclinic phase at higher temperature will consistent with the (binary) phase diagram of Sm_2O_3, wherein the monoclinic phase is preferred at higher temperatures. Therefore the cubic phase is being favored at lower temperatures.

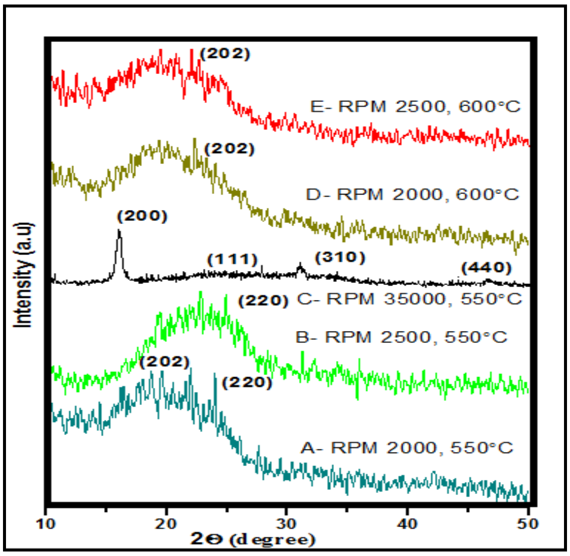

Fig 1. XRD spectra of Samarium Oxide thin films prepared with different rpm and annealing temperature

FTIR Analysis

Fig 2 (A-E) shows the Fourier Transform Infrared spectra of Sm_2O_3 thin films. The shallow peak is

centered at 528 cm^{-1} is ascertained due to stretching vibration of Sm_2O_3 molecules present in the prepared thin films. This existence is irrespective of all rpm and annealed temperatures. A kink at 843 cm^{-1} and the sharp peak at 109 cm^{-1} are assigned due to ν-CO_3^{2-} present in the sample which may be due to the preparation of the sample in open atmospheric condition [12, 19]. A weak band at 1401cm^{-1} and a shoulder at 1519 cm^{-1} can be assigned due to stretching vibration of C=C and C-N functional groups present in the basic compounds of Poly Vinyl Pyrrolidone (PVP). A broad and weak band at 2915 cm^{-1} has been assigned due to C-H stretching vibration of PVP. A strong and broad band at 3510 cm^{-1} and a very sharp band at 3727 cm^{-1} are due to ν-OH vibrations.

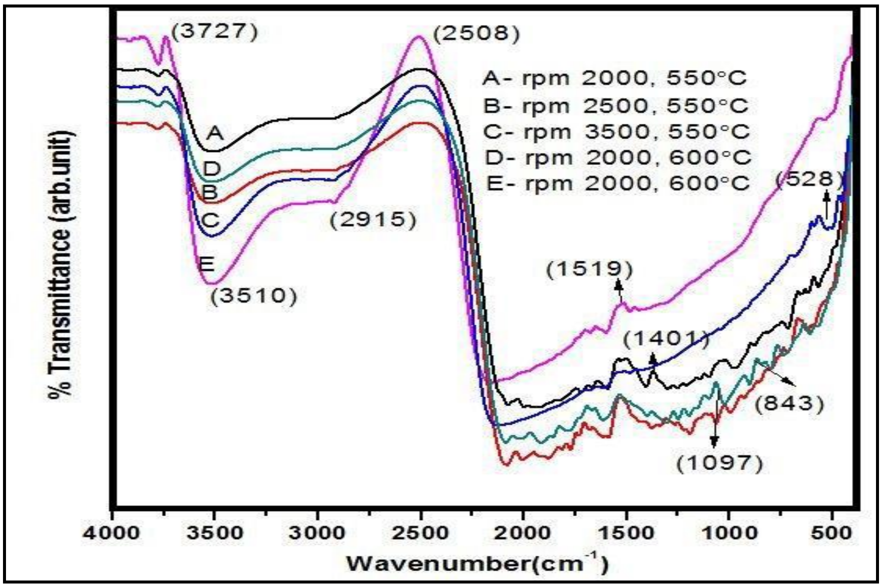

Fig 2. FTIR spectra of prepared thin films at various rpm and annealing temperature

Raman Spectroscopic Analysis

Raman active phonons spectra of various rpm and annealed temperature spin coated Sm_2O_3 films structure again confirmed by the XRD analysis report (Fig 1). This confirmation is good agreement with White and Keramidas and Gouteronet.al., [20-21]. Moreover 4 of all the 21 Raman active modes were predicted by group theory for B-type Sm_2O_3 structure were also observed. The observed lines at 457 cm^{-1} ,335 cm^{-1}, 152 cm^{-1} can be assigned to A_g modes and 424 cm^{-1}can be assigned to B_g and A_g modes [22-24].

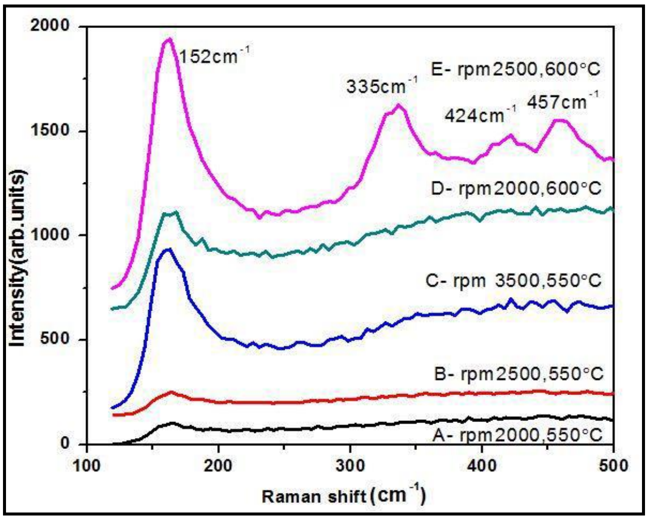

Fig 3. Raman of Samarium oxide thin films at different rpm and annealing temperature

UV-Vis Spectroscopic Analysis

The spectral distribution of absorbance was measured at nearly normal incidence in the wavelength range 300-1100 nm for the Sm_2O_3 films deposited at different temperatures and at different rpm is shown in fig(4) (A-E). From the fig. (4), it is found that in the visible region, the films have good absorbance. In the IR region the absorbance decreases and the films became transparent. Further it is observed that the absorption increases with increase in rpm for the films deposited at 550° C and 600° C. It is also observed that, the absorption edge is shifted to the longer wavelength side (red shift). This is attributed that, the 4f-5d electronic transitions had occurred in the Sm^{+2} ions. These time of bands have shown that some Sm^{+2} ions were converted into Sm^{3+} ions. This also explains the observed increase in the UV region 326nm and the decrease of intensity of the absorption bands are situated in between 300 nm and 500 nm. So, this UV-Vis spectroscopic data show the conversion of the Sm^{3+} to Sm^{2+} species in the same time with oxidation processes of oxygen.

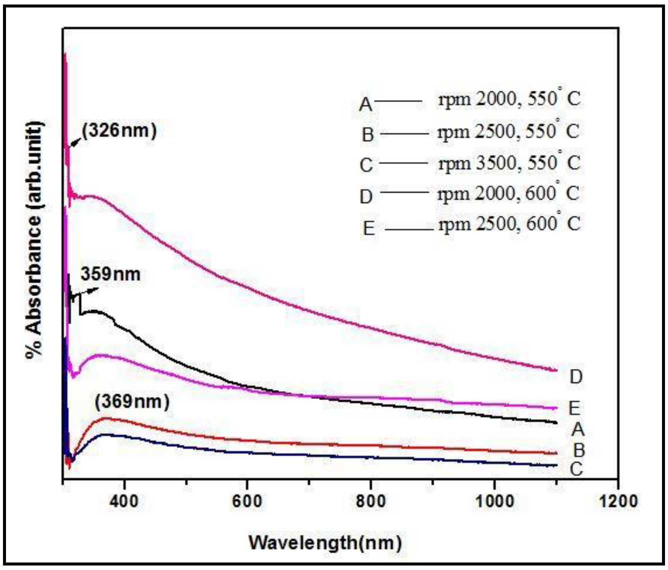

Fig 4. The absorption spectra of Samarium oxide thin film at different rpm and annealing temperature

The optical band gap for the above films has been calculated from the relation between absorption coefficient (α) and the incident photon energy (hν) [15]. The plots of (αhν) versus hν for the Sm_2O_3 films deposited at different annealing temperatures and different rpm is shown in fig. (5). Extrapolation of the linear portion to $(\alpha h\nu)^2=0$ gives the direct allowed band gap values for the deposited films. The energy gaps of the prepared thin films are found in between 3.15 eV to 3.48 eV.

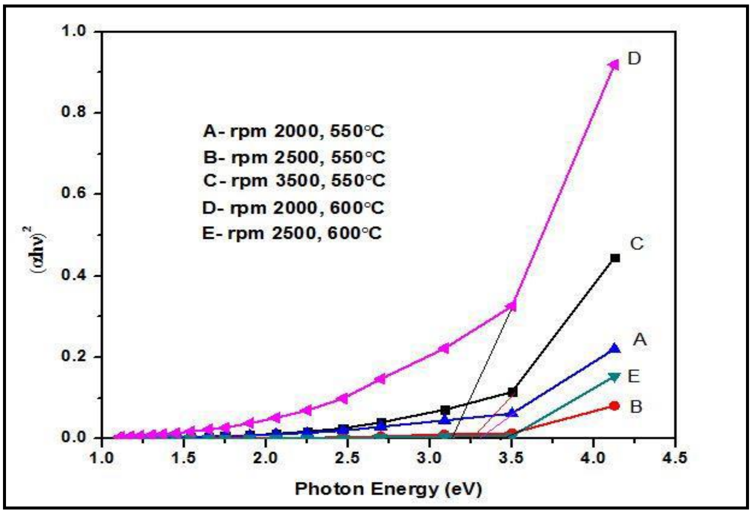

Fig 5. The optical band gap of samarium oxide thin films with various rpm and annealing temperatures

Photoluminescence study

The PL spectra of Sm_2O_3 films deposited on glass substrate at different temperatures and at different rpm are shown in fig 6. A broad band observed at 435 nm is due to the strong emission originated from shallow donor levels of oxygen vacancies present in valence band levels of Sm. The low energy peak is observed at 411 nm. The other weak peaks at 462 nm are due to pronounced donor-acceptor pair transition and its phonon replicas and the other relatively strong UV peak which is caused by optical replicas.

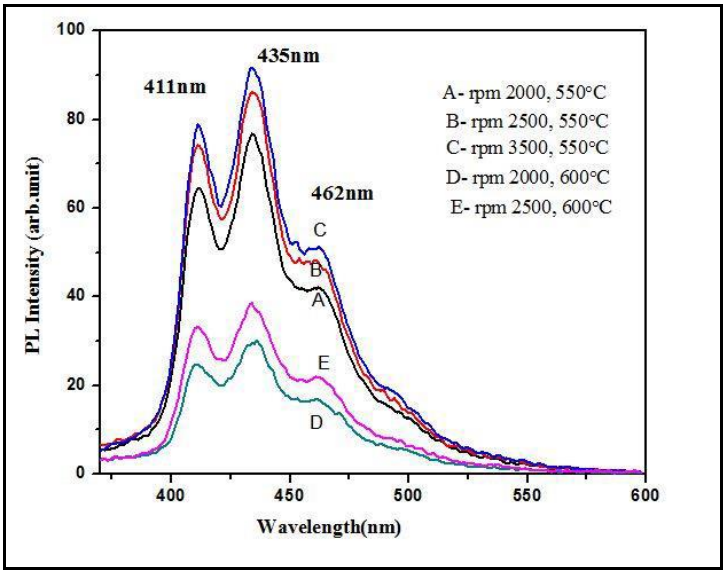

Fig 6. PL spectra of Sm_2O_3 films prepared at different temperatures and at different rpm

Conclusion

Sm_2O_3 thin films fabricated on glass substrate by sol-gel spin coating with different rpm successfully. The X-ray diffraction patterns of deposited thin films exhibited an amorphous nature at low temperature and transferred the polycrystalline state at above 550° C. Raman active modes of spin coated thin films revealed obviously B-type of Samarium oxide. This is confirmed by X-ray diffraction analysis due to an effect of annealing temperature. The stretching vibration of Sm_2O_3 at 540 cm^{-1} was detected by Fourier Transform Infrared Spectroscopy. The coated Samarium oxide thin films are transparent at low energy of visible region and an excellent absorbency at higher energy of UV region. The calculated optical band gap of coated thin films has varied in between 3.15eV to 3.48 eV.

References

1. Rozhkov VA, Trusove A.YU, Berezhov IG. Silicon MIS structures using samarium oxide films. Thin Solid Films, 1988, 325; 151.
2. Rozhkov VA, Goncharov VP, Trusove YU. in:IEEE 5^{th} International Conference on Conduction and Breakdown in Solid Dielectric. 1995, 552.
3. Sanghum J, Kiju I, Hyundoek Y, Hyelan L, Hyunjun S, Sangmu C, Taesung J, Hyunsang H. in IEDM Technical Digest, 2001, 20.6.1-20.6.2.
4. Dakhel AA. Dielectric and Optical properties of Samarium Oxide thin films. J.Alloys Compd., 2001, 365; 233-239.
5. Chang IYK, Hwang YR, Juan Pc, Lee JYM. Temperature dependence of the current conduction mechanisms in Sm_2O_3 thin films. J.Electrochem.Soc., 2008, 15;G265-G268.
6. Hwang YR, Chang IYK, Wang MT, Lee JYM. The fabrication and characteristic of metal-oxide-silicon capacitors and field-effect transistor using Dy_2O_3 and Sm_2O_3 gate dielectrics, Integrated Ferroelectrics. An Int.J. 2008, 97; 111-120.
7. Pan TM, Hung CC, You SX, Yeh CC, Effect of annealing on the structural and electrical properties of high-k Sm_2O_3 dielectrics. Electrochem.Solid State Lett., 2008, 11; G62-G65.

8. Wu MH, Cheng CH, Lai Cs, Pan TM, Structural properties and sensing performance of high-k Sm_2O_3 membrane-based electrolyte-insulator-semiconductor for pH and urea detection. Sens. Actuators., 2009, 138;221-227.
9. Pan TM, Huang CC. Influence of post deposition annealing on structural properties and electrical characteristics of thin Sm_2O_3 and Ti_2O_7 dielectrics. J.Appl.Surf.Sci., 2010, 256; 2786-2791.
10. Paivassari J, Niinisto J, Myllymaki P, Dezelah C, Winter C, Putkonen M, Nieminen M. A comparative study on lanthanide oxide thin films grown by Atomic layer deposition. Thin solid films, 2005, 472; 1-2.
11. Ono H, Katsumata T. Interfacial reactions between thin rare-earth-metal oxide films and Si substrates. J.Appl.Phys., 2003, 93; 6393.
12. Shalini K, Shivashankar S. Oriented growth of thin films of Samarium oxide by MOCVD. J.Bull.Mater.Sci., 2005, 28; 49-54.
13. Leskela M, Kukli K, Ritala M. Rare earth oxide thin films for gate dielectrics in microelectronics. J.Alloys Compd., 2006, 418; 27-34.
14. JCPDF Card No. 74-1807.
15. Lixiong Yin, Huang Jainferg, Huang Yan, Cao Liyun. Oriented growth and optical properties of Samarium Oxide thin films. J.Adv.Mater.Res., 2010, 105; 345-347.
16. Gin-ya Adachi and NobuhitoImanaka. The Binary Rare Earth Oxides. Chem.Rev., 1998, 98; 1479-1514.
17. Baker RT, Gomex-Sainero LM, Metcalfe IS. Pretreatment of Induced Nanostructural Evolution in Cerium oxide, Samarium oxide and CeO_2/Sm_2O_3 supported pd catalysts for intermediate temperature Methanol fuel cells. J.Phys.Chem., 2009, 113;12465-12475.
18. WenChiao Chin, Kuan Yew Cheong. Effects of post deposition annealing temperature and ambient on RF magnetron sputtered Sm_2O_3 gate on n-type silicon substrate.J.Mater.Sci., 2011, 22; 1816-1826.
19. Peng Liu, Yunjia Wang, Xue Wang, Chao Yang. Polypyrrole-coated Samarium oxide nanobelts: fabrication, characterization and application in super capacitors. J.Nanopart.Res., 2012, 14; 1232.
20. White WB, Keramidas VG. Raman spectroscopic study of the Rare earth sesquisulfieds. Spectrachem.Acta.,1992, 28A.
21. Gouteron J, Michel D, Lejus AM, Zarembowithch J. Raman spectra of lanthanide sesquioxide single crystals. J.Solid.State.Chem., 1981, 38; 288-296.
22. Martel JF, Jandal S, Lejuss AM. Optical crystal field study of Sm_2O_3 (C- and B-type). J.Alloy and Compd., 1998, 275-277; 353-355.
23. Jack Silver and Robert Withnall. Probes of structural and Electronic Environmens of Phosphor activators:Mossbauer and Raman spectroscopy. Chem Rev., 2004, 104; 2833-2855.
24. Terushia Hong, Ken-ichikondo, Kazutaka, Xlakmura. High pressure Raman Spectroscopic study of structural phase transisiton in Sm_2O_3. J. Mater.Sci., 2007, 42; 2582-2585.

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