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Structural, spectroscopic and electrical properties of CeO_2 thin films prepared by simple and economical sol-gel technique

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Abstract

Uniform, multilayered and good quality CeO_2 thin films were prepared on glass and silicon substrates by economical and efficient sol-gel spin coating technique. The precursor, solvent and complexing-chelating agent used in the process were Cerium Nitrate Hexahydrate, 2-Methoxy ethanol and Acetyl Acetone respectively. The films were characterized at different temperatures. The optical reflectance increased with increase in annealing temperature. In the temperature range of 100^oC-500^oC, the refractive index of the film increased from 1.72-2.06. The optical band gap decreased with the increase in annealing temperature. MOS capacitors were fabricated using the films coated on Silicon substrate. The Capacitance-Voltage (C-V), Current-Voltage (I-V) and dissipation-Voltage (tanδ-V) measurements were made at various annealing temperatures. The dielectric constant and resistivity were found to be high. The dependence of dielectric constant, current density and resistivity of MOS devices on annealing temperatures was studied and discussed. The current density decreased but the resistivity increased with increase in annealing temperature.

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Keywords: CeO_2 Thin films; Sol-gel route; MOS devices

1. Introduction

Ceria is an excellent rare-earth oxide that has displayed potential for various applications like gas sensors [1], catalyst [2], photocatalyst [3], dye sensitized solar cells [4], electrochromic devices [5], dielectric thin film material in CMOS [6] and coatings on optical devices [7]. The wide range of applications of CeO_2 is attributed to a host of its beneficial properties such as wide optical band gap (3-3.6eV), high refractive index (n=2.2-2.3), matching lattice constant with Si ($\Delta a < 1\%$), low density of interface states ($<10^{11} cm^2 eV^{-1}$), high dielectric constant (23-52) and small equivalent oxide thickness (3.8^{o}A) [8-13]. CeO_2 is being considered one among the alternative metal oxides to SiO_2 for designing silicon based electronic devices [14].

Numerous techniques are in vogue for preparing CeO_2 thin films. Catalina Mansilla [15] investigated the structure, microstructure and optical properties of CeO_2 thin films prepared by combined e-beam evaporation and ion beam assisted deposition technique. It was found that the all films showed cubic structure and the films prepared by ion assisted deposition technique exhibited higher density, smaller grain size, a high expansion of lattice constant, higher refractive indices and lower band-gaps. Balakrishnan et al [16] deposited CeO_2 thin films on silicon substrate by pulsed deposition technique and reported cubic structure with a change in preferred orientation from (100) to (200), an increase in refractive indices and Band gap as the substrate temperature increased. King et al [17] prepared CeO_2 thin films by atomic layer deposition technique using tetrakis Cerium and reported the dependence of structure and dielectric relaxation behavior of these films on growth temperature. Grosse et al [18] studied the conductivity and dielectric properties of CeO_2 thin films between two gold electrodes on a STO substrate and reported the room temperature dielectric constant ε_r to be ~ 26.9.

In thin film preparation, sol-gel method has several distinct merits over other techniques. Possibility of producing consistent and high quality films, low equipment cost, scope of controlling composition and coating large curved surfaces and conservation of energy due to room temperature preparation are a few advantages of the sol-gel technique. Anees A Ansari [19] prepared CeO_2 thin films by sol-gel dip coating process using Ammonium Cerium Nitrate as the precursor. He observed a particle size of 3-4nm for the films annealed at 650^{o}C, direct band gap of 3.23eV and strong PL band at 378nm.

In the present work, we have prepared homogeneous and uniform CeO_2 thin films on glass and p-type Si (100) substrates by sol-gel spin coating technique. MOS capacitors have been fabricated using these films coated on silicon substrates. The structural, optical, dielectric and electrical properties of these films have been investigated at different annealing temperatures. The objective of the present paper is to estimate the optical parameters like reflectance, transmittance, refractive index, optical band-gap of CeO_2 thin films in the UV-Visible range and dielectric parameters like dielectric constant, leakage current density and resistivity of the MOS structures as a function of temperature.

2. Experimental technique

Cerium Nitrate Hexahydrate was used as the precursor, 2-Methoxy ethanol as the solvent, Acetyl Acetone as the complexing and chelating agent. To prepare 0.5M CeO_2 sol, stoichiometric amount of Cerium Nitrate Hexahydrate was taken in a 100ml glass beaker and to this 50 ml of 2-Methoxy ethanol was added. This mixture was rigorously stirred using a magnetic stirrer. The stirring continued for 30 minutes till the precursor dissolved completely. To this, Poly Ethylene Glycol (PEG) and Acetyl Acetone was added while stirring. PEG was used to enhance the viscosity of the sol. The volume ratios of the solvent, PEG and complexing-chelating agent are 60:6:1. The solution was stirred overnight. The sol obtained was filtered using Whatman filter paper to remove any particulates that could have formed and subsequently aged for 24 hrs to facilitate the completion of hydrolysis. The CeO_2 sol was then stored in a air tight plastic container.

Special glass was cut into pieces of dimensions of 1.5 cm X 1.5cm using a diamond cutter. These glass substrates were pre-cleaned with soap solution and water at first. Then they were subjected to subsequent ultra-sonication in DI water, acetone and were washed with DI water respectively. Finally they were dried in a hot-air oven at 70^{o}C for 45 minutes. The cleaned and dried substrates were then placed in the spin coating chamber. A few drops of 0.5M CeO_2 sol was placed on the clean glass substrates using a micropipette. The substrate was then spun at 2500 rpm for 60 sec. The resulting thin films were pre-heated for 10 minutes at 60^{o}C. The coating and pre-heating was repeated 5 times to obtain films of sufficient thickness. These films were then annealed at different temperatures for 1 hr each. At various temperatures, the UV reflectance and transmittance was measured in the wavelength range 300 nm-1100 nm.

MOS capacitors were prepared using CeO_2 thin films deposited on p-Si (100) wafers with a resistivity of 1-10Ωcm. Prior to the deposition of films, the silicon wafer was cut into regular 1cm X 1cm square pieces. These silicon pieces were subjected to standard Radio Carporation of America (RCA) cleaning procedure. RCA-1solution was prepared with NH_3, H_2O_2 and DI water (NH_3: H_2O_2: DI water=1:1:5) and was heated to 75 ^{o}C. The cut silicon pieces were kept in this solution for 15 min while maintaining the temperature at 75^{o}C. Then to remove the native oxides that could be present on these wafers, these silicon pieces were washed with dilute HF (HF:DI H_2O= 1:10). RCA-2 solution was prepared with HCl, H_2O_2 and DI water (HCl: H_2O_2: DI water=1:1:6) and was heated to 75 ^{o}C. The cut silicon wafers were kept in this solution for 15 min to remove metal contamination while maintaining the temperature at 75^{o}C. Then the wafers were dried at 50^{o}C in an oven. After spin coating and pre-heating the CeO_2 films five times on the pre-cleaned silicon substrates, films were annealed at 400^{o}C, 600^{o}C and 800^{o}C for 3 hr respectively. These films were patterned with top aluminium gate electrodes using shadow mask and aluminium contact layer on the backside by thermal evaporation.

The structural details of the films were studied using Bruker X-ray Diffractometer (Model: Bruker AXS D8 Advance). The surface morphology of the films was studied using Scanning Electron Microscope (Model: Ultra 55 FESEM). The topography and the surface roughness of the films were ascertained using Atomic Force Microscope (A.P.E.Research A-100). The thickness of the films was measured using optical profilometer (Model: Zeta

Instruments Zeta-20). The optical studies of the films were carried out using UV-VIS-NIR spectrophotometer (Model: HR400, Ocean Optics, USA) that has an accuracy of ±5% both in reflectance and transmittance mode. The C-V, tanδ-V and I-V characterizations were done using Agilent Impedance Analyzer 4294A and Agilent Device Analyzer B1500A (Model: SUSS Microtec PM5 Probe station) respectively.

3. Results and Discussion

3.1. Structural Properties

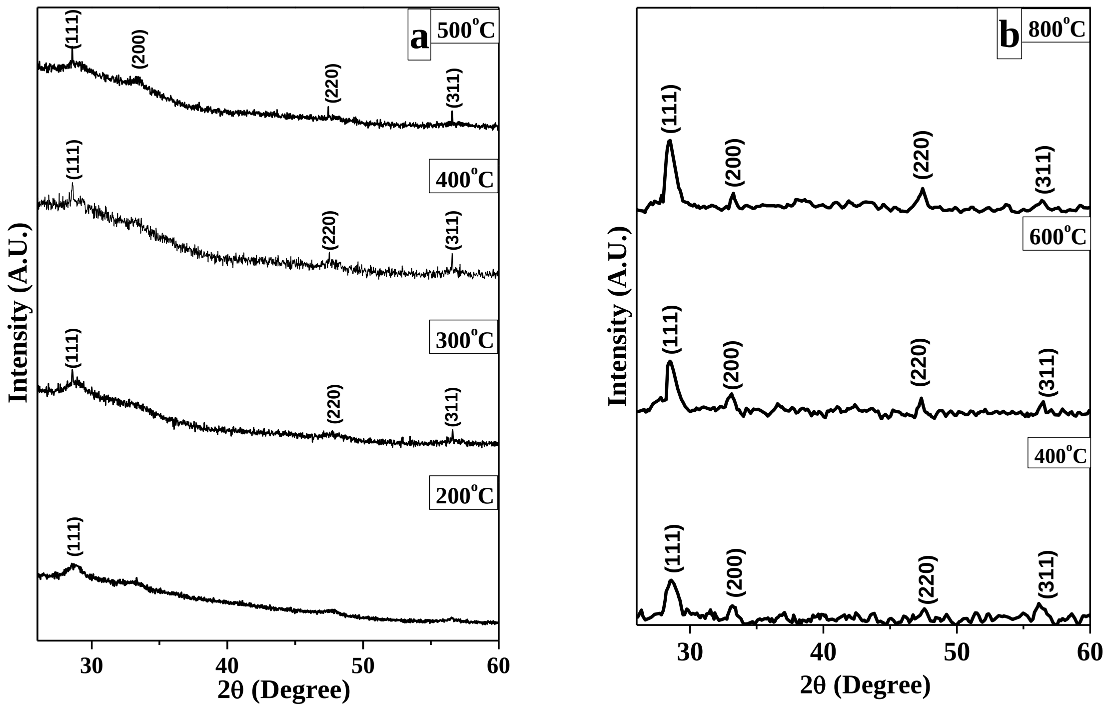

Fig.1(a, b): XRD pattern of CeO_2 thin films coated on (a) glass substrates and annealed at different temperatures for 1hr (b) silicon substrates and annealed at different temperatures for 3hr.

The XRD pattern of CeO_2 thin films deposited by sol-gel method and annealed at temperatures 200°C-500°C for 1 h (deposited on glass substrates) and annealed at temperatures 400°C-800°C for 3 h each (deposited on silicon) are shown in Fig.1 (a, b) respectively. From the Fig.1(a) it was observed that the XRD pattern of CeO_2 thin film annealed at 200°C/1 h has a single low intensity peak at 28.5°, suggesting the beginning of crystallization. XRD pattern of CeO_2 films annealed at 400°C and 500°C for 1 h each showed small peaks at 2θ= 28.59°, 33.13°, 47.56° and 56.43°. These peaks were indexed as (111), (200), (220) and (311) planes. The peaks for CeO_2 thin films annealed at 400°C/1 h and 500°C/1 h were slightly sharper and narrower indicating better crystallinity at higher temperatures. However, the increase in crystallinity with temperature was quite small. The absence of secondary peaks was an evidence to the phase purity of the films.

Fig.1 (b) showed well defined diffraction peaks at the very 2θ positions mentioned above. The XRD peak positions obtained in the present work are in good agreement with JCPDS card # 65-5923 and reports [9, 19], confirming the cubic fluorite structure of CeO_2 films. With the increase in annealing temperature, narrower and sharper peaks were noticed. The grain size was calculated by using Debye-Scherrer equation,

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

Where D is the particle size, λ is the wavelength of Cu-Kα radiation, θ is the diffraction angle and β is the full width at half maximum (FWHM) of XRD peaks. The mean grain sizes in the CeO_2 thin films annealed at 400^oC, 600^oC and 800^oC for 3 h were 8 nm, 11 nm and 16 nm respectively. It was noticed that with the increase in temperature, the particle size increased slightly.

3.2. Morphological Properties

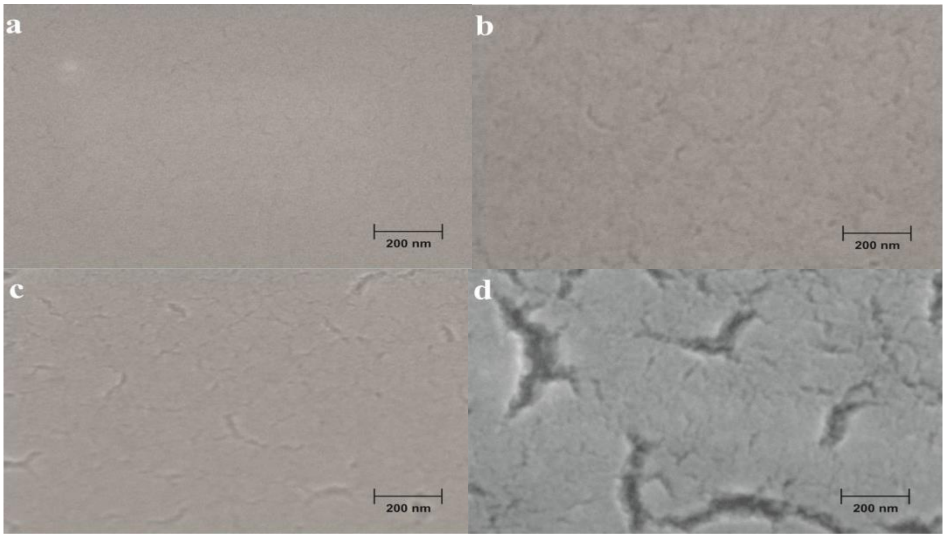

Fig. 2 (a-d): SEM images of CeO_2 thin films annealed at (a) 400^oC/1hr (b) 500^oC/1hr (c) 600^oC/3hr (d) 800^oC/3hr

The surface morphology of CeO_2 thin films annealed at 400^oC/1hr, 500^oC/1hr, 600^oC/3hr and 800^oC/3hr are shown in Fig.2 (a-d). The SEM images of the films annealed at 400^oC/1hr and 500^oC/1hr showed uniform structure. The SEM micrographs of the films annealed at 600^oC/3hr and 800^oC/3hr showed very slight crystallization. It was observed that as the annealing temperature increased, fine cracks were developed on the surface of the film. The number and size of the cracks increased as the annealing temperature increased. Hence the CeO_2 film annealed at 800^oC/3hr developed more cracks.

3.3. AFM studies

The AFM micrographs of CeO_2 films conventionally annealed at different temperatures are shown in Fig.3(a-d). The scan size of these micrographs is 5μm X 5μm). The AFM images revealed very slight crystallization in the films conventionally annealed at 400°C/1 h and 500°C/1 h. The micrographs of CeO_2 films annealed at 600°C/3 h and 800°C/3 h showed closely situated grains with voids in between. The surface roughness of the conventionally annealed CeO_2 films showed a small increase as the annealing temperature increased. The surface roughness R_a of films annealed at 400°C/1 hr, 500°C/1 hr, 600°C/3 hr and 800°C/3 hr are 0.779 nm, 0.985 nm, 1.26 nm and 1.98 nm respectively.

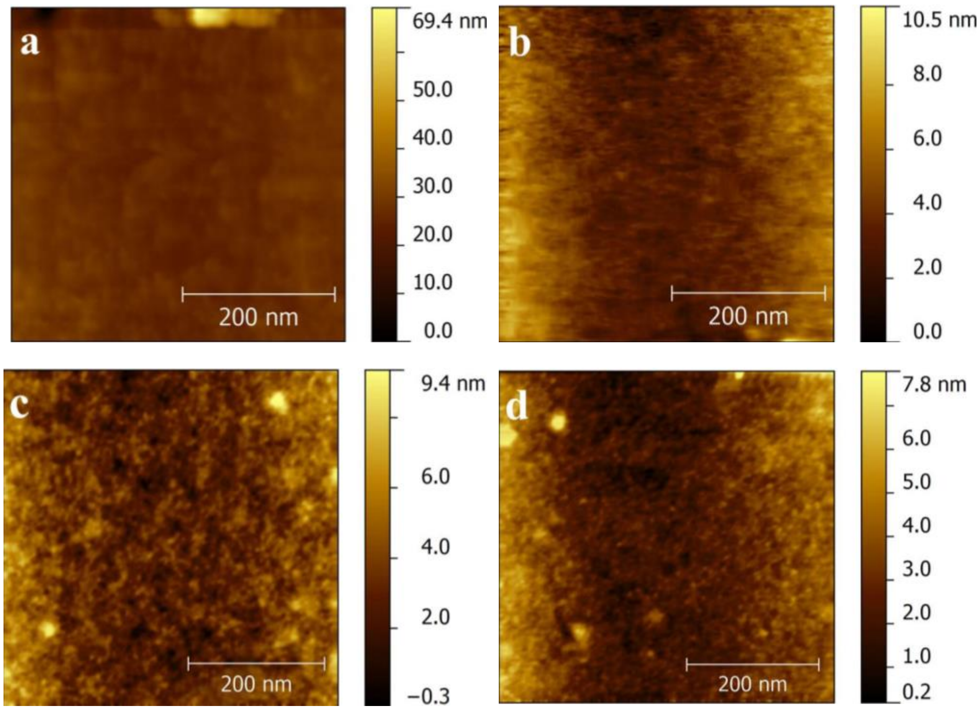

Fig.3 (a-d): AFM micrographs of CeO_2 thin films conventionally annealed at (a) 400°C/1 hr (b) 500°C/1 hr (c) 600°C/3hr (d) 800°C/3hr

3.4. Optical Properties

From Fig.4 (a) it was observed that conventionally annealed CeO_2 films showed good transmittance in the visible and NIR regions. The transmittance of the as- prepared CeO_2 thin film at a wavelength 600 nm was nearly 87%. It was observed that the transmittance maxima decreased with the increase in annealing temperature. As the annealing temperature increased to 500°C, the transmittance decreased to approximately 78% at 600 nm. The drop in the transmittance with the rise in annealing temperature may be due to densification of the films.

Fig.4 (b) showed that the reflectance of the as-prepared CeO_2 thin films was very close to that of bare glass. But it increased with the increase in annealing temperature after 200°C. This is due to the improved density of the films. Also, the reflectance was found to be maximum in the higher wavelength range. The refractive index of the films n_f was calculated was calculated in the wavelength range 350 nm-730 nm from the reflectance spectra using the formula [20],

$$n_f = \left[n_o n_s \; \frac{1+\sqrt{R_{max}}}{1-\sqrt{R_{max}}}\right]^{1/2} \text{ -- (2)}$$

Where n_o and n_s denote the refractive indices of the ambient medium and the substrate, R_{max} represents the maximum reflectance in the reflectance curve. The values of refractive index and the thickness of the as-prepared and the annealed films have been tabulated in Table.1.

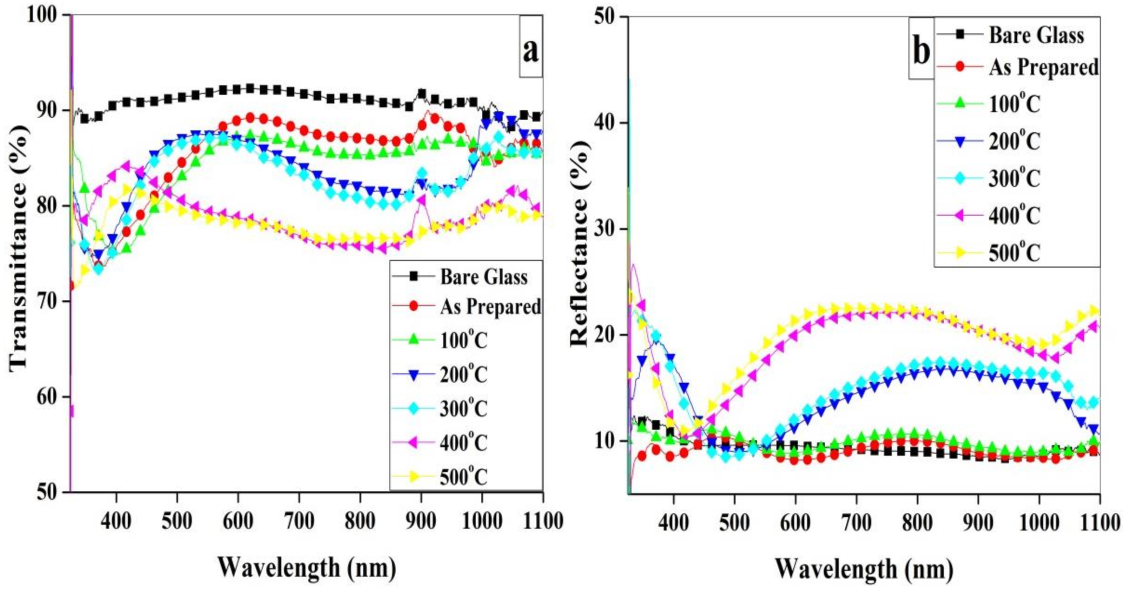

Fig.4 (a) Transmittance spectra (b) Reflectance spectra of CeO_2 thin films deposited on glass and conventionally annealed at various temperatures

Table.1

Refractive index and thickness of the films determined from the reflectance spectra at various annealing temperatures.

Annealing temperature (^oC)	Wavelength (nm)	Refractive index of the film n_f	Film thickness (nm)
As prepared	473.25	1.72	350
100^oC	471.05	1.75	330
200^oC	373.62	1.97	162
300^oC	333.56	2.03	134
400^oC	722.93	2.04	126
500^oC	722.93	2.05	122

The increase in the refractive index of the CeO_2 films with the increase in annealing temperature can be attributed to the change in the microstructure. The decrease in thickness of the films is due to the evaporation of solvent.

The optical band gap of CeO_2 thin films have been calculated by Tauc's method [21] using the relation,

$$(\alpha h\nu)^n = B\,(h\nu - E_g) \qquad (3)$$

Where α is the absorption coefficient, B is a constant, E_g is the optical energy gap and n=2 for direct band gap transitions. Variation of $(\alpha h\nu)^2$ as a function of photon energy hν for the as-prepared and annealed CeO_2 thin films is shown in Fig.5. By extrapolating the linear portion of the plot onto the energy axis gives points at which the absorption coefficient is zero. The optical band gap is obtained from the intercept values on the energy axis. The optical band gap of the as-prepared film and the films annealed at 300^oC and 500^oC are found to be 3.29 eV, 3.04 eV and 2.69 eV respectively. It was observed that the optical band gap decreased with the increase in annealing temperature. M.Y.Chen et al [22] have reported the optical band gap of the as-prepared and 900^oC annealed CeO_2 thin films deposited on saphphire substarte by rf magnetron sputtering to be 2.53 and 2.91eV respectively. D.Barreca et al [23] reported the refractive index values of 2.79±0.05 at 6328 ^{o}A and optical band-gap values of 2.8±0.1 and 2.4±0.1eV for CeO_2 thin films by plasma-enhanced CVD technique with and without O_2 in the plasma. B.P.Gorman et al [24] reported refractive index values in the range 1.75-2.3 for CeO_2 thin films [24].

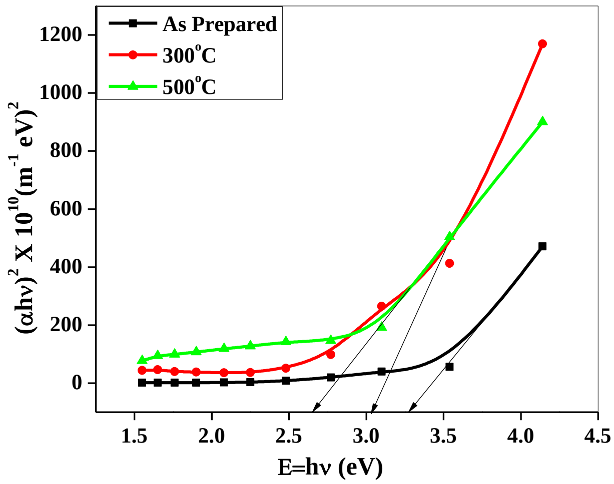

Fig.5. Optical band gap estimation of the as-prepared and annealed CeO_2 thin films.

3.5. Dielectric Properties

3.5.1. C-V Characteristics

The MOS capacitors were fabricated using CeO_2 thin films. The area of the top electrodes used was 0.2060 X 10^{-3} cm^2. The C-V characteristics of these devices using CeO_2 thin films annealed at 400°C and 600°C at a signal frequency of 1MHz are shown in Fig.6. The oxide capacitances at 1MHz for films annealed at 400°C and 600°C for 3hr in air ambient are 44.9PF and 101PF for film thicknesses 102 nm and 94 nm respectively. The variation of oxide capacitances with increase in signal frequency are depicted in Fig.7. A shift in the flat band voltage V_{FB} to a higher gate voltage at higher frequency could be due to the interface traps [25].

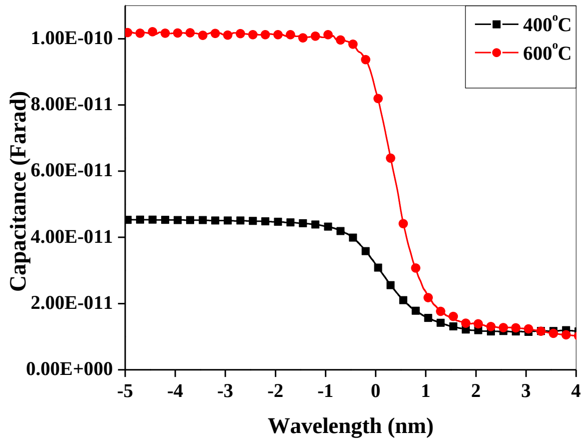

Fig.6.C-V characteristics of CeO_2 thin films annealed at (a) 400°C (b) 600°C for 3hr in air ambient.

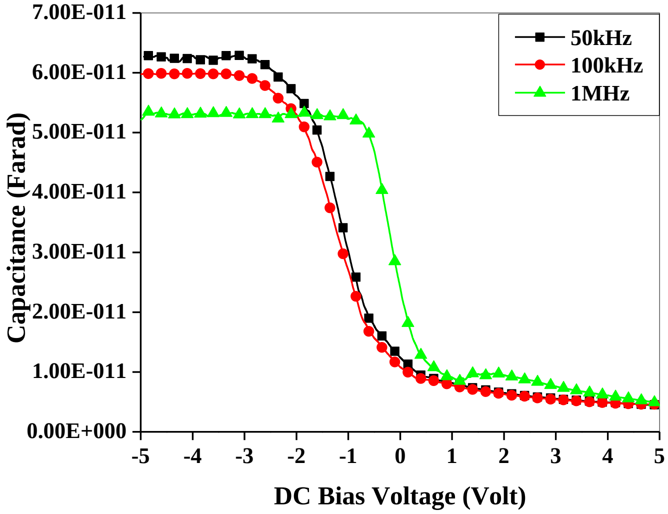

Fig.7. Frequency dependence of accumulation capacitance of CeO_2 thin films annealed at 800°C for 3hr in air ambient.

For the CeO_2 thin films annealed at 400°C, 600°C and 800°C, the dielectric constants were 25.1, 52.03 and 26 respectively at 1MHz frequency. For the thin film annealed at 600°C, the value of dielectric constant was found to be high. This could be attributed to the enhanced crystallization in the film. The decrease in the dielectric constant for the film annealed at 800°C could be speculated to be because of the fine cracks developed in the film during crystallization. Jyrki Lappalainen et al [25] reported the dielectric constant for CeO_2 thin film prepared by PLD technique and deposited on n-type Si substrate to be 23. Logothetidis et al [6] reported a high dielectric constant of ε_r ~90 for CeO_2 thin films prepared by electron beam evaporation technique at a substrate temperature of 950°C. Soo Kiet Chuah et al [26] reported the dielectric constant values of 4.66, 4.23, 3.84 and 3.84 for CeO_2 thin films deposited on silicon substrate by rf magnetron sputtering and post-annealed at 400°C, 600°C, 800°C and 1000°C respectively. In this report, a decreasing trend is observed for dielectric constant with increase in temperature.

3.3.2. I-V characteristics

The Current-Voltage plots of CeO_2 thin films annealed at 400°C, 600°C and 800°C for 3hr in air ambient are shown in Fig.8 (a,b) respectively. The thicknesses of these films are 102 nm, 94 nm and 88 nm respectively. Using an electrode area of 0.2060 X 10^{-3} cm^2, the values of current density and resistivity have been estimated at 4V. For the CeO_2 thin films annealed at 400°C, 600°C and 800°C, the calculated values of the current density are 18.05 X 10^{-4} Acm^{-2}, 7.81 X 10^{-6} Acm^{-2} and 1.23 X 10^{-6} Acm^{-2} and the values of resistivity are 0.217 X 10^9 Ω cm, 5.49 X 10^9 Ω cm and 370 X 10^9 Ω cm respectively. It was observed that the current density has decreased but the resistivity increased with the increase in annealing temperature.

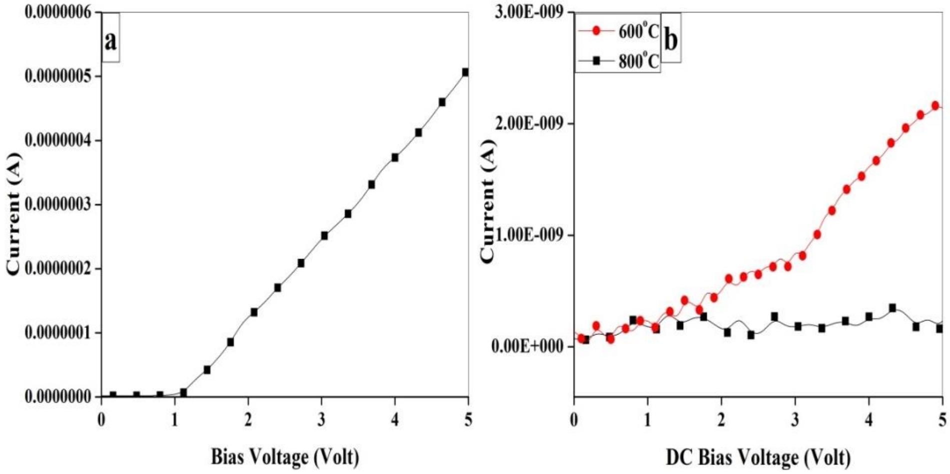

Fig. 8 (a,b): I-V characteristics of CeO_2 thin films conventionally annealed at (a) 400°C (b) 600°C and 800°C for 3 hr

The variation of loss tangent with bias voltage at 400°C and 600°C are shown in Fig.9. At a bias voltage of 4V, the value loss tangent for CeO_2 films annealed at 400°C and 600°C were found to be 0.031 and 0.024 respectively. As the dielectric loss is extremely less, the CeO_2 thin films are deemed to be appropriate to use in device fabrication.

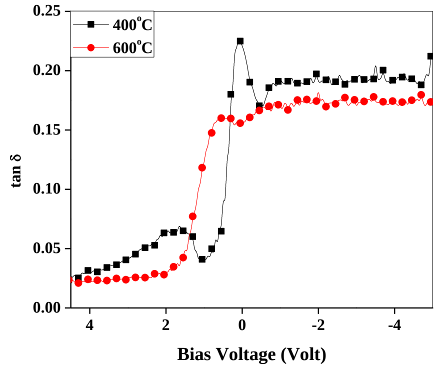

Fig.9. tanδ-V plot of CeO_2 films annealed at 400°C and 600°C for 3hr in air ambient.

4. Conclusions

Uniform, stable and high-quality CeO_2 thin films were prepared by sol-gel method. The XRD pattern established cubic fluorite structure of CeO_2. The reflectance and hence the refractive index of the films increased with increase with annealing temperature. The optical band gap decreased from 3.29eV to 2.69eV when annealing temperature increased from 70°C to 500°C. MOS capacitors were fabricated using CeO_2 thin films annealed at various temperatures. The Capacitance-Voltage (C-V), Current-Voltage (I-V) and Loss tangent-Voltage (tanδ-V) characterizations were studied and dielectric constant, current density and resistivity were calculated. The values of dielectric constants and the resistivity of the CeO_2 films annealed at different temperatures were fairly high, proving the films to be suitable for MOS capacitor fabrication.

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References

[1].Yixin Liu, Yu Ding, Lichun Zhang, Pu-Xian Gao, Yu Lei, RSC Advances 2 (2012) 5193–5198.
[2].Yu Zhang, Fei Hou, Yiwei Tan, Chem. Commun, 48, (2012) 2391–2393.
[3].Sher Bahadar Khan, M. Faisal, Mohammed M. Rahman, Aslam Jamal Science of the Total Environment 409 (2011) 2987–2992.
[4].Hua Yu, Yang Bai, Xu Zong, Fengqiu Tang, G. Q. Max Lu, Lianzhou Wang, Chem. Commun 48 (2012) 7386–7388.
[5].Y. Li, X. Dong, J. Gao, D. Hei, X. Zhou and H. Zhang, Phys. E 41 (2009) 1550–1553.
[6].S. Logothetidis, P. Patsalas, E.K. Evangelou, N. Konofaos, I. Tsiaoussis, N. Frangis, Materials Science and Engineering B 109 (2004) 69-73.
[7].K. Narasimha Rao, L. Shivlingappa, S. Mohan, Materials Science and Engineering B 98 (2003) 38-44.
[8].S. Guo, H. Atwin, S.N. Jacobsen, K.Jarrendahl, U. Helmersson, Journal of Applied physics. **77 (**1995**)**5369-5376.
[9].M.T. Ta, D. Briand, Y. Guhel, J. Bernard, J.C. Pesant, B. Boudart, Thin Solid Films 517 (2008) 450–452.
[10].S. Deshpande, S. Patil, S. V. Kuchibhatla, S. Seal, Applied Physics Letters 87, (2005) 133113:1-3.
[11].F.C. Chiu, S.Y.Chen, C.H.Chen, H.W. Chen, H.S. Huang, H.L.Hwang, Japan. Journal of Applied Physics 48 **(**2009**)** 04C014:1-4.
[12].T. Yamamoto, H. Momida, T. Hamada, T. Uda, T. Ohno, Thin Solid Films, 486, (2005) 136-140.
[13].Y. Nishikawa, N.Fukushima, N.Yasuda, K .Nakayama, S .Ikegawa, Japanese Journal of Applied Physics Part l 41 (2002)2480-2483.
[14].Fu-Chien Chiu, Electrochemical and Solid-State Letters, 11 (6) (2008) H135-H137.
[15].Catalina Mansilla, Solid State Sciences 11 (2009) 1456–1464.
[16].G. Balakrishnan , S. Tripura Sundari, P. Kuppusami , P. Chandra Mohan, M.P. Srinivasan, E. Mohandas, V. Ganesan, D. Sastikumar, Thin Solid Films 519 (2011) 2520–2526.
[17].P.J. King, M. Werner, P.R. Chalker, A.C. Jones, H.C. Aspinall, J. Basca, J.S. Wrench, K. Black, H.O. Davies, P.N. Heys Thin Solid Films 519 (2011) 4192–4195.
[18].V.Grosse, R Bechstein, F Schmidl, P Seidel, Journal of Physics. D: Applied Physics 40 (2007) 1146–1149.
[19].Anees A. Ansari, Journal of Semiconductors Vol. 31, No. 5 (2010) 053001:1--5.
[20].K. Narasimha Rao, T. S. Radha, M. Ramakrishna Rao, Journal of Indian Institute of Science, Vol. 58, No. 7 (1976) 315 – 29.
[21].B. Elidrissi, M. Addou, M. Regragui, C. Monty, A. Bougrine, A. KachouaneThin Solid Films 379 (2000) 23-27.
[22].M.Y. Chen, X.T. Zu, X. Xiang, H.L. Zhang, Physica B 389 (2007) 263–268.
[23].D. Barreca, G. Bruno, A. Gasparotto, M. Losurdo, E. Tondello, Materials Science and Engineering C 23 (2003) 1013–1016.
[24].B.P. Gorman, V. Petrovsky, H.U. Anderson, T. Petrovsky, Journal of Materials Research 19 (2004) 573-578.
[25]. Jyrki Lappalainen, Darja Kek, Harry L. Tuller, Journal of the European Ceramic Society 24 (2004) 1459–1462.
[26].Soo Kiet Chuah, KuanYew Cheong, Zainovia Lockman, Zainuriah Hassan, Materials Science in Semiconductor Processing 14 (2011) 101– 107.