On the wettability and optical properties of nanocrystalline CeO$_2$ thin films

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Cerium oxide (CeO$_2$) is an inexpensive material and has many applications due to its excellent wetting and optical properties. However, deposition of CeO$_2$ thin films of desired wettability (hydrophobic/hydrophilic) and with high refractive index ($n$) and large band gap ($E_g$) is a challenging task. In the present study, wettability and optical properties of E-beam evaporated CeO$_2$ thin films have been reported in the substrate temperature range RT-700 °C. All the evaporated CeO$_2$ thin films showed only hydrophobic nature, as revealed by contact angle measurements. Further, the maximum values of $n$ (2.38) and $E_g$ (3.21 eV) of CeO$_2$ thin film are obtained at 700 °C as determined by spectroscopic ellipsometer. Our earlier reported results of sputtered CeO$_2$ thin films show that it is possible to achieve both hydrophilic and hydrophobic nature and also high $n$ (2.62) and large $E_g$ (3.43 eV) values simply by varying the substrate temperature and this phenomenon has been attributed to the occurrence of energetic ion bombardment of depositing films. These results indicate that the wettable and optical properties of CeO$_2$ thin films depend on the deposition technique and the associated process parameters.

Keywords: CeO$_2$ thin films, Nanocrystalline, E-beam evaporation, Wettability, Optical properties

1 Introduction

The wettability of materials is divided into two categories; depending on the solid surface engineering: hydrophobicity and hydrophilicity$^1$. The presence of either phenomenon can be explained by wetting behavior, which may be classified by measuring water contact angle on the solid surface of interest$^2$. The contact angle is important wherever the intensity of the phase contact between liquid and solid substances needs to be checked or assessed. Metal oxides with particular hydrophobic characteristics have many research applications in corrosion prevention, liquid conveyance, self-cleaning surfaces, and among other fields. Hydrophilic characteristics too used for self-cleaning application and have few additional advantages like they can chemically break down adsorbed dirt when exposed to light (as photocatalysis process), as a surface segregating additives (to create high surface porosity) and antifogging$^{3,4}$. Among rare earth oxides cerium oxide (CeO$_2$) is an inexpensive and the most studied material, and is widely used in many applications such as polishing materials, automotive exhaust catalysts, gas sensors, electrolyte materials, oxygen storage, oxide fuel cells$^{5,10}$. et al.$^{11,12}$ have reported that the CeO$_2$ film coated on magnesium alloy by a simple immersion process at room temperature (RT) with respect to pH of the solution and process time shows superhydrophobic property. Liang et al.$^{13}$ have also demonstrated superhydrophobicity of CeO$_2$ coated on aluminum substrates by immersion growth process for wide range of related process parameters. Azimi et al.$^{14}$ reported the hydrophobic nature of sputtered CeO$_2$ films but no processing details are available. Jain et al.$^{15}$ have also reported the hydrophobic nature of CeO$_2$ films deposited by DC sputtering using Ce metal target as a function of target to substrate distance. In our recent reported work$^{16}$ it has been observed that the wettability of the sputtered CeO$_2$ films varies from hydrophobic to hydrophilic with respect to increasing substrate temperature. To the best of our knowledge no report is available on the wetting properties of nanocrystalline CeO$_2$ thin films deposited by E-beam evaporation. The E-beam evaporation technique enables deposition of films at temperatures from RT to high temperatures, and the film has main advantages of high purity, controlled thickness, large area uniformity and the film can also be deposited over a wide variety of substrates.

Further, CeO$_2$ is also suitable for microelectronics as a high-k gate oxide materials, various optical, electro-optical and optoelectronic devices due to its unique properties such as moderate band gap (3.2 to 3.6 eV),
high refractive index (2.2 to 2.8) and high dielectric constant (23-26)\(^1\)\(^-\)\(^19\). The optical properties of nanocrystalline CeO\(_2\) thin films are well studied by many previous reports in theory and experiment providing different values of the refractive index (\(n\)) and the optical band gap (\(E_g\))\(^20\)\(^-\)\(^30\). Patsalas et al.\(^31\) reported the optical properties of nanocrystalline ceria films deposited by ion beam assisted E-beam evaporation technique from RT to 950 °C and observed the values of \(n\) varying from 1.65 to 2.15 and the values of \(E_g\) varying from 2.4 to 2.8 eV, which are not close to that of standard values, perhaps due to improper ion energy, causing oxygen deficiency in the deposited films. Anwar et al.\(^32\) also reported the value of \(n\) at 600 nm increasing from 1.78 to 2.1 as the substrate temperature increased from RT to 400 °C for nanocrystalline ceria thin films deposited by E-beam evaporation, but these studies are limited to low substrate temperature. In our recent reported work\(^16\) it has also been observed that in case of sputtered CeO\(_2\) films, the values of \(n\) and \(E_g\) increase with increasing substrate temperature, and high \(n\) (2.62) and large \(E_g\) (3.43 eV) values are obtained that are quite close to that of standard values.

Keeping in view of the above said facts in the present work, we have carried out the investigations on wettable and optical properties of E-beam evaporated CeO\(_2\) thin films with respect to the substrate temperature and compared the results with our earlier reported data for sputtered CeO\(_2\) thin films.

### 2 Experimental Procedure

For this study, CeO\(_2\) powder (99.99%, Alfa Aesar) was used for the preparation of CeO\(_2\) thin films. Trichloroethylene (TCE), methanol, acetone and HF (All are semiconductor grade, Merck Ltd, Germany) chemicals were used for cleaning the substrates. Prior to the deposition the Si (100) substrates were first degreased with boiling TCE and then followed by acetone, methanol and de-ionized water cleaning. After that the substrates were dipped in 10% HF for 10 sec to remove native SiO\(_2\) layer, followed by de-ionized water cleaning. An in-house designed and fabricated E-beam evaporation system was used for the deposition of nanocrystalline CeO\(_2\) thin films at different substrate temperatures varying from RT to 700 °C. CeO\(_2\) powder was evaporated from a graphite boat at 120 W E-beam gun power and the substrate was kept at a distance of 8 inch from the source material. The evaporation chamber was evacuated to about 1×10\(^{-6}\) mbarr pressure using diffusion pump along with liquid N\(_2\) trap backed by rotary vacuum pump.

The structural properties of CeO\(_2\) thin films were characterized by an X-ray diffractometer (Bruker, Germany, model: D8-Avalance), using Cu K\(\alpha\) radiation at 1.54 Å in 0-20 geometry. The morphology and surface roughness were studied using Atomic force microscopy (AFM, model Multimode-V, Vicco Instrument) over 1µm×1µm area. The optical properties of CeO\(_2\) thin films were analyzed by Spectroscopic ellipsometer (J A Woollam, model: VASE32) in the wavelength range 250-1200 nm for the incident angles 65° and 75°. The thicknesses of CeO\(_2\) thin films were also measured using Stylus profiler (Ambios, model: XP-200). The contact angles of CeO\(_2\) thin films were recorded by Sessile drop method (Dataphysics, Model OCA15EC) to determine the wetting behavior of deposited thin films.

### 3 Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of nanocrystalline CeO\(_2\) thin films deposited on Si (100) substrate at RT and 700 °C, and also CeO\(_2\) powder. The XRD results show that for the deposited films the crystal structure of CeO\(_2\) corresponds to the cubic fluoride structure (JCPDS No. 81-0792) of the source CeO\(_2\) powder. Thin film deposited at room temperature shows polycrystalline nature with no preferred orientation and at 700 °C substrate temperature it shows only dominant (111) orientation. The crystallite size of deposited thin films was calculated using well known Debye-Scherrer formula\(^33\). The crystallite size related to (111)
orientation is found to increase from 11.6 nm to 23.9 nm and corresponding value of FWHM decreases from 0.69° to 0.34° with increasing substrate temperature from RT to 700 °C. These results clearly show that the increase of substrate temperature is in favor to the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favorable positions, resulting in the enhancement of the crystallinity.

Figure 2 shows the 2D and corresponding 3D AFM images over 1 µm × 1 µm area of nanocrystalline CeO$_2$ thin films deposited at different substrate temperatures (a) RT, (b) 600 °C, (c) 650 °C and (d) 700 °C, respectively. The AFM images show dense and uniform distribution of grains with smooth surface morphology for the films deposited at high substrate temperature in comparison to the film deposited at RT. From the AFM images it is observed that the average surface roughness for the substrate temperatures below 650 °C is in the range 2.0-2.5 nm. However, the surface roughness has been found to reduce about 1.0 nm for the substrate temperature of 700 °C.

Wetting properties of nanocrystalline CeO$_2$ thin films are studied by contact angle measurement and are shown in Fig. 3. A surface coating represents hydrophobic nature if the contact angle is $\theta > 90^\circ$ or hydrophilic, if it is $\theta < 90^\circ$. The wetting property of CeO$_2$ thin films showed highest contact angle value of 106.88° for the film deposited at RT and the value of

![2D and corresponding 3D AFM images of CeO$_2$ thin films deposited at different substrate temperature (a) RT, (b) 600 °C, (c) 650 °C and (d) 700 °C, respectively.](image)

![Contact angle measurement images of CeO$_2$ thin films deposited at (a) Room temperature and (b) 700 °C.](image)
contact angle decreased to 92.42° when the substrate temperature increased from RT to 700 °C. It is to be noted that all the deposited nanocrystalline CeO$_2$ thin films in our study have showed hydrophobic nature for a wide substrate temperature range from RT to 700 °C. The microstructure and surface roughness of the deposited CeO$_2$ film may play important roles in determining the wettability. However, it is unlikely in our case that surface roughness plays a role in wettability due to its very low values (1.0 to 2.5 nm) as observed above from AFM results. Thus, it is attributed to the films microstructure. In our earlier reported work on the sputtered CeO$_2$ films, it has been observed that with respect to increasing substrate temperature the wetting properties of the deposited films vary from hydrophobic to hydrophilic at substrate temperature 700 °C. This observed difference in the wettable property CeO$_2$ films deposited at 700 °C in both evaporation and sputtering techniques can be understood on the basis of the underlying mechanisms in the film deposition process. In the case of sputtering process the heavy energetic Ar$^+$ ions in the plasma gain energy and actively participate in film growth through sputtering, atomic mixing, densification, enhanced migration of adatoms and field enhanced diffusion via charging and restructuring. The ionic bombardment of the energetic ions on the growing film leads to the creation of various metastable states/structures due to thermal spike, and the film properties also depend on the energies of the impinging ions. Thus, for the CeO$_2$ film grown even at same 700 °C by sputtering or E-beam evaporation process the film density and microstructure are expected to be quite different and thus may show up different properties.

The optical properties of CeO$_2$ thin films were studied by Spectroscopic ellipsometer (SE). Figure 4 represents the SE data for the ellipsometric parameters (phase ψ & angle Δ) of the CeO$_2$ thin films deposited at 700 °C for the incident angles 65° and 75°. The experimental data has been fitted using Tauc-Lorentz (TL) model for the air/CeO$_2$/Si which takes into account the film thickness and contribution of the substrate. The solid line in the figure represents the model-fit data and it can be seen that all the features present in the experimental spectra are reproduced by the model fits. The fitting parameters within the parametric dispersion model yields thickness of CeO$_2$ thin films about 60±0.5 nm. These thicknesses are in good agreement with thicknesses 62±2 nm) measured by the stylus profiler.

Figure 5 represents the refractive index (n) as a function of wavelength as obtained from the ellipsometric data of CeO$_2$ thin films deposited at different substrate temperatures. In the inset of Fig. 5 we have plotted the value of n at fixed wavelength of 600 nm.
600 nm for the comparison and it was observed that the value of $n$ increases from 1.99 to 2.38 with the increase in substrate temperature from RT to 700°C. The optical band gap of the films is calculated using the well known Tauc relation $\alpha h\nu = A(h\nu - E_g)^n$, where $A$, $E_g$, $h\nu$ and $n$ are the probability parameter for the transition, band gap of the material, incident photon energy and the transition coefficient (2 for indirect and 1/2 for direct band gap), respectively. The absorption coefficient $\alpha$ is extracting from the ellipsometric data. The indirect band gap of the CeO$_2$ thin films was evaluated by extrapolating the straight line part of the curves $(\alpha h\nu)^{1/2} = 0$ as shown in Fig. 6. For the clarity of presentation we have shown the graphs of CeO$_2$ thin films deposited at RT and 700°C. Inset of Fig. 6 shows the variation of optical band gap ($E_g$) with respect to the substrate temperature. The calculated value of $E_g$ was found to increase from 3.12 to 3.21 eV with increase of the substrate temperature from RT to 700 °C. The observation of $n$ and $E_g$ with respect to the temperature could be due to improvement in low packing density, partial crystallinity of the film and low adatom mobility of the film and increase in crystallite size when the film deposited at high substrate temperature. It is to be noted that although these observed $n$ and $E_g$ values at 700 °C are close to that of the standard values, but still a little less than that obtained in our earlier reported work for sputtered CeO$_2$ films (2.62 and 3.43 eV), and this can be understood on the basis of occurrence of energetic ion bombard in sputtering technique, as explained above$^{19,35,36}$.

Thus, our studies indicate that both wettability and optical properties of CeO$_2$ thin films strongly depend on the deposition technique and the process parameters. Magnetron sputtering technique has an added advantage of inherent ion assisted process to tailor the wettability and optical properties as desired.

4 Conclusions

Nanocrystalline CeO$_2$ thin films were deposited on Si (100) substrates by E-beam evaporation technique at different substrate temperatures in the range RT-700 °C. All the deposited CeO$_2$ films exhibited only hydrophobic property in the entire range of substrate temperatures. We have achieved the values of refractive index and optical band gap of the deposited CeO$_2$ thin films close to that of the standard values for the films deposited at 700 °C. Over all our studies indicate that the wettability and optical properties depend on the process technique and the related process parameters. Further, magnetron sputtering technique enables to deposit CeO$_2$ films with either hydrophobic or hydrophilic and also with high refractive index and large band gap simply by varying the substrate temperature. The occurrence of energetic ion bombardment in sputtering technique is an added advantage to achieve the desired wettability and optical properties.

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