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Effect of substrate temperature on nanocrystalline CeO_2 thin films deposited on Si substrate by RF magnetron sputtering

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ABSTRACT

Single oriented nanocrystalline CeO_2 thin films have been deposited over Si (100) substrate by RF magnetron sputtering in the temperature range 600-700 ^{o}C, using CeO_2 target. X-ray diffraction pattern for the as deposited CeO_2 film at 700 ^{o}C shows the dominant (111) orientation with corresponding FWHM value of 0.378^{o} and the crystallite size 21.50 nm. The refractive index and the optical band gap both were found to increase from 2.35 to 2.66 and 3.25 to 3.43 eV, respectively with increasing substrate temperature. Atomic force microscopy results reveal highly smooth surface of the deposited films with surface roughness below 1.15 nm for the entire range of deposition temperatures. Further, the contact angle measurements on the as deposited CeO_2 films showed variation from 122.36 to 81.67^{o} with respect to the substrate temperature, transforming the wetting property from hydrophobic to hydrophilic in nature. These results indicate the possibility of producing CeO_2 films with varying properties for various device applications simply by controlling the substrate temperature. Copyright © 2015 VBRI Press.

Keywords: CeO_2 thin films; nanocrystalline; RF magnetron sputtering; ellipsometer; contact angle.

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Introduction

Cerium oxide (CeO_2), also called as ceria, is one of the most studied and useful functional rare earth oxides. CeO_2 is an excellent and desired buffer layer material for the epitaxial growth in many applications such as for high temperature superconducting and semiconductor thin films due to its small lattice mismatch, good stability and similar thermal coefficient with these materials **[1-3]**. It has many other potential practical applications to the field of fluorescence, magnetic, photocatalysis materials and as high oxygen storage capacity, gas sensors, and as solid oxide fuel cells due to its ability to absorb and release oxygen easily and to exhibit higher ionic conductivity at lower temperatures **[4-9]**. CeO_2 is also suitable for various optical, electro-optical and optoelectronic devices because it is transparent oxide in the visible and near-IR spectral region **[10-11]**. Keeping in view of wide applications of CeO_2 thin films efforts have been put by several workers for its deposition on various substrates such as glass, quartz, Si, Al_2O_3, and Ni by different techniques viz E-beam evaporation, DC/RF magnetron sputtering, pulsed laser deposition (PLD), and molecular beam epitaxy (MBE) **[12-20]**.

The properties of materials like optical, electrical, mechanical, catalytic etc. get changed with changing grain size from bulk to nanocrystalline thin films and play an important role in the device applications. The optical properties of CeO_2 thin films have been reported by various groups providing different values for the refractive index (n) and the optical band gap (E_g). Patsalas *et al.* **[21]** reported the optical properties of nanocrystalline ceria films deposited by E-beam evaporation technique at various temperatures between RT to 950 °C. They showed the value of n varies from 1.65 to 2.15 and band gap value varies from 2.8 to 2.0 eV. Recently, Anwar *et al.* **[18]** also reported the value of n at 600 nm increases 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 technique. Balakrishnan *et al.* **[22]** reported the optical properties of nanocrystalline ceria thin films prepared by PLD and showed that the values of n and E_g increased from 2.2 to 2.6 and 3.4 to 3.6 eV, respectively with increasing substrate temperature from RT to 700 °C. On the other hand by PLD technique Nie *et al.* **[20]** reported the E_g value from 3.01 to 3.26 eV.

Surface engineering often involves directing the wettability of materials, and is divided into two categories depending on the desired situation: hydrophobicity and hydrophilicity **[23]**. The presence of either phenomenon may be explained by wetting behavior, which may be classified by measuring water contact angle (WCA) on the surface of interest **[24]**. The contact angle is important wherever the intensity of the phase contact between liquid and solid substances needs to be checked or assessed. Metallic oxides with particular wettability characteristics have far research applications in corrosion prevention, liquid conveyance, and self-cleaning surfaces, among other fields. A few reports are available on the wettability of CeO_2 films. Recently, Jain *et al*. **[25]** have reported the wettability of CeO_2 films deposited by DC sputtering using Ce metal target, and observed the hydrophobic nature, with the contact angle values in the range 94.86-104.09° as a function of target to substrate distance (5-7 cm). Among various thin films deposition techniques, RF/DC magnetron sputtering has been recognized as a promising versatile technique for the deposition of stoichiometric film of metal oxides. Its main advantages are good adhesion to substrates, and high density and homogeneity of deposited films. Moreover it permits large scale deposition of high quality films at high deposition rates. However, there is no systematic study available on the optical and wettable properties of nanocrystalline CeO_2 thin films deposited by RF magnetron sputtering technique using CeO_2 target.

Experimental

Materials

CeO_2 (99.99%, China Rare Metal Material, China) target and Ar (99.999%, BOC, India) gas have been used for the preparation of CeO_2 samples. Trichloroethylene, methanol, acetone and HF (All are semiconductor grade, Merck Ltd, Germany) chemicals were used for cleaning the substrates.

Method

Nanocrystalline CeO_2 thin films about 50 nm thick have been deposited at different substrate temperatures in the range of room temperature (RT) to 700 °C on Si (100) substrate using CeO_2 target in an in-house designed and fabricated downstream RF magnetron sputtering system. The substrates were first degreased in boiling trichloroethylene (TCE), then followed by acetone methanol, and de-ionized water cleaning. After that the substrate was dipped in 10% HF for 10 sec to remove the native SiO_2 layer, followed by rinsing in de-ionized water. The RF sputtering power and deposition pressure were kept fixed at 200 W and 30 mTorr, respectively for the deposition of CeO_2 thin films. A turbo-based pumping system, backed by roots and rotary pumps, was used to achieve a base pressure below 2×10^{-6} Torr. Ar was used as sputtering gas. The distance between the sputtering target and substrate was fixed at 5 cm. The deposition pressure in the vacuum chamber was measured by a compact process ion gauge (Pfeiffer) and the gas flow rate (15 sccm) was accurately controlled by mass flow controllers (Aalborg, model: GFC-17).

The structural properties of CeO_2 thin films were characterized by an X-ray diffractometer (Bruker, Germany, model: D8-Avalance), using Cu Kα radiation at 1.54 Å in θ-2θ 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 studied by Spectroscopic ellipsometer (J.A. Woollam, model: VASE32) and the optical parameters were calculated including the information on pseudo-dielectric functions in the wavelength range 250-1200 nm, for the incident angles 65° and 75°. The thickness of CeO_2 samples was measured using a Stylus profiler (Ambios, model: XP-200). Contact angles of CeO_2 thin films were recorded on Drop shape analysis system (model DSA10MK2 from Kruss GmbH, Germany).

Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the as deposited nanocrystalline CeO_2 thin films deposited on Si (100) substrate at different substrate temperatures varying from RT to 700°C. The films deposited at RT show (111) and (220) peaks with no preferred orientation. The film deposited at 600°C shows dominant (111) orientation. It can be seen that the intensity of (111) peak increased as the substrate temperature increases further upto 700°C.

The crystallite size (d) of the films was calculated using Scherer formula **[26]**,

$$d = \frac{0.9\lambda}{B\cos\theta_B}$$

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where λ, θ_B and B are the X-ray wavelength (1.54Å), Bragg diffraction angle and line width at half-maximum (FWHM), respectively. It depicts that with increase in substrate temperature there is a decrease in FWHM corresponding to (111) XRD peak and an increase in crystallite size due to increase in crystallinity. The value of FWHM was found to decrease from 1.22^o to 0.378^o and the corresponding crystallite size was increased from 6.65 to 21.50 nm with increasing the substrate temperature from RT to 700^{o}C as shown in **Table 1**. These results show that the increase of substrate temperature is in favour to the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favourable positions, resulting in the enhancement of the crystallinity.

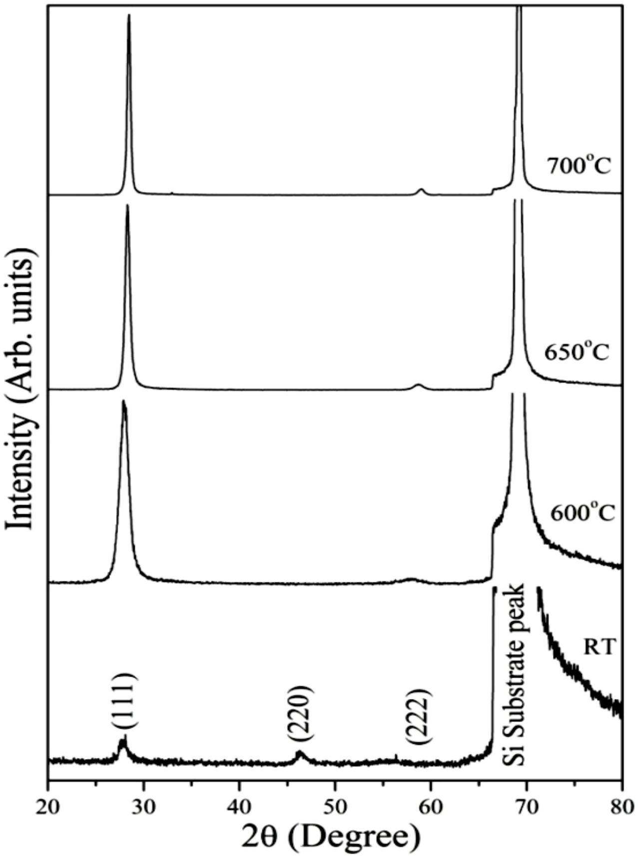

Fig. 1. X-ray diffraction pattern of CeO_2 thin films deposited on Si (100) substrate at different substrate temperatures.

Table 1. Various calculated parameters of nanocrystalline CeO_2 thin films deposited on Si substrate.

Substrate temperature (ºC)	RT	600	650	700
FWHM (degree)	1.22	1.13	0.59	0.38
Crystallite size	6.65	7.15	13.81	21.20
Refractive index @ 600 nm	2.32	2.40	2.42	2.62
Optical Band gap (eV)	3.25	3.30	3.36	3.43
Contact angle (degree)	122.36	93.97	90.33	81.67

Fig. 2 show the 2D and corresponding 3D AFM images over 1µm×1µm area of nanocrystalline CeO_2 thin films deposited at different substrate temperature. The AFM images showed dense and uniform distribution of grains with smooth surface morphology of the thin films deposited at high substrate temperatures in comparison to the thin film deposited at room temperature. The average root mean square (RMS) surface roughness of all the samples are below 1.15 nm and the average grain size was found to increase with an increase in the substrate temperature from 600 to 700^{o}C. These AFM results are in good agreement with XRD results.

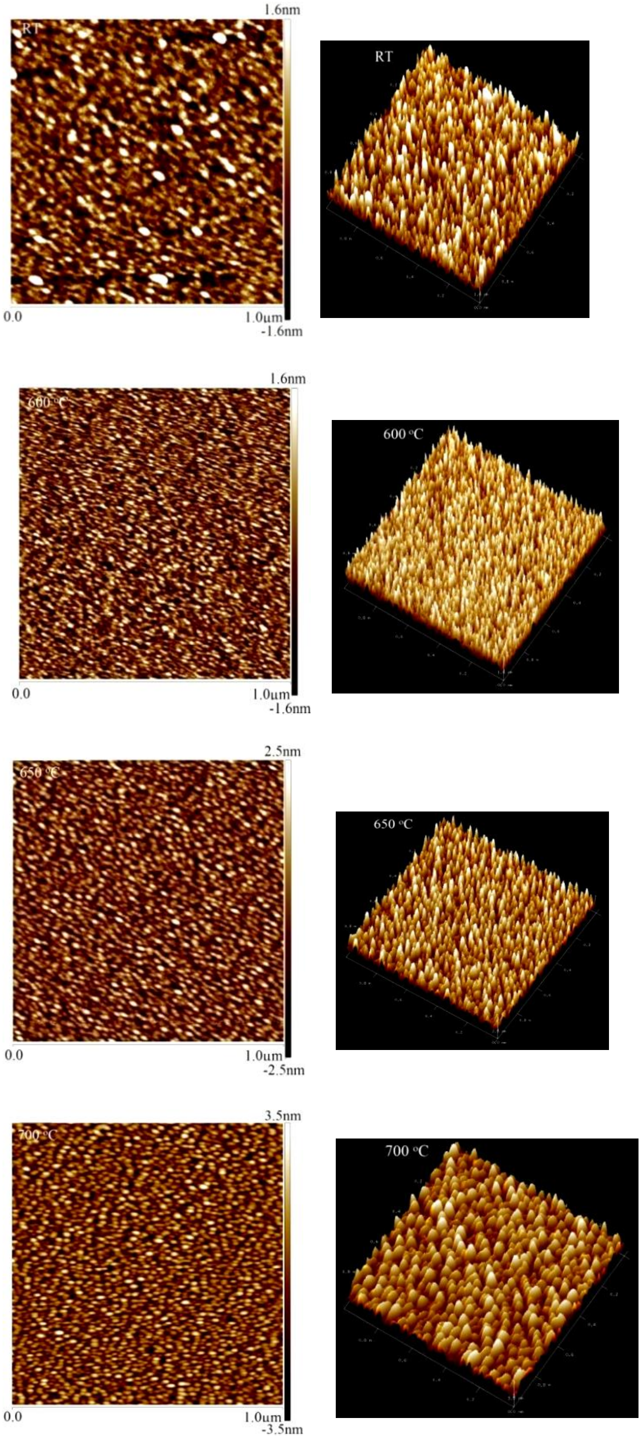

Fig. 2. 2D and corresponding 3D images of CeO_2 thin films deposited at different substrate temperatures.

The optical properties of CeO_2 thin films were studied by Spectroscopic ellipsometer (SE) in the wavelength range of 250-1200 nm. SE measurements provide the data related

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to the ellipsometer angle Ψ and phase Δ with respect to wavelength or photon energy. It is a non-destructive model fitting based technique, which minimizes the difference between measured experimental and calculated fitting values as a function of wavelength.

In the case of transparent CeO_2 films, the measured quantity is the pseudo-dielectric function <ε(w)>, which also takes into account the thickness of the film due to the multiple reflections from the film-substrate interface **[27]**. **Fig. 3** represents the SE data for the ellipsometric parameter (Ψ) of the CeO_2 thin films deposited at 700°C for the incident angles 65^o and 75^o, respectively. The experimental data has been fitted using Tauc-Lorentz (TL) model for the air/CeO_2/Si structure 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 fit. The fitting parameters within the parametric dispersion model yields thickness of CeO_2 thin films about 50±0.5 nm. These thicknesses are in good agreement with thicknesses 52.5±2 nm) measured by the stylus profiler.

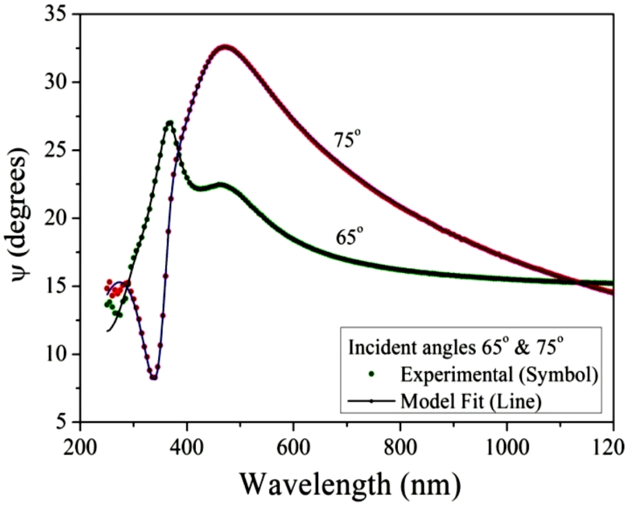

Fig. 3. Experimental and model fitted ellipsometric parameter (Ψ) of CeO_2 thin films deposited at 700°C. Solid line indicates model fit.

Fig. 4 shows real $<\varepsilon_1>$ and imaginary part $<\varepsilon_2>$ of the pseudo-dielectric function, as extracted from the SE data of CeO_2 thin films deposited at 700°C. For the clarity of presentation, the spectrum recorded for the incident angle of 75^o is shown here. The solid line in the figure represents the model-fit data well matched with the experimental spectra (represents by symbol).

Fig. 5 represents the refractive index (n) as a function of wavelength in the range of 250-1200 nm as obtained from the corresponding ellipsometric data of CeO_2 thin films deposited at different substrate temperatures. The results show that the value of refractive index strongly depends on the deposition conditions. The value of refractive index at 600 nm wavelength increases from 2.32 to 2.62 with an increase in substrate temperature from RT to 700°C as shown in the inset of **Fig. 5** and summarized in **Table 1**. The reported refractive index of CeO_2 thin films and single crystal are 2.2 to 2.6 and 2.4 to 2.56, respectively **[21, 22, 28]**. The low values of refractive index observed in our case at room temperature could be due to low packing density, partial crystallinity of the film and low adatom mobility of the film which are improved when the film deposited at high substrate temperature.

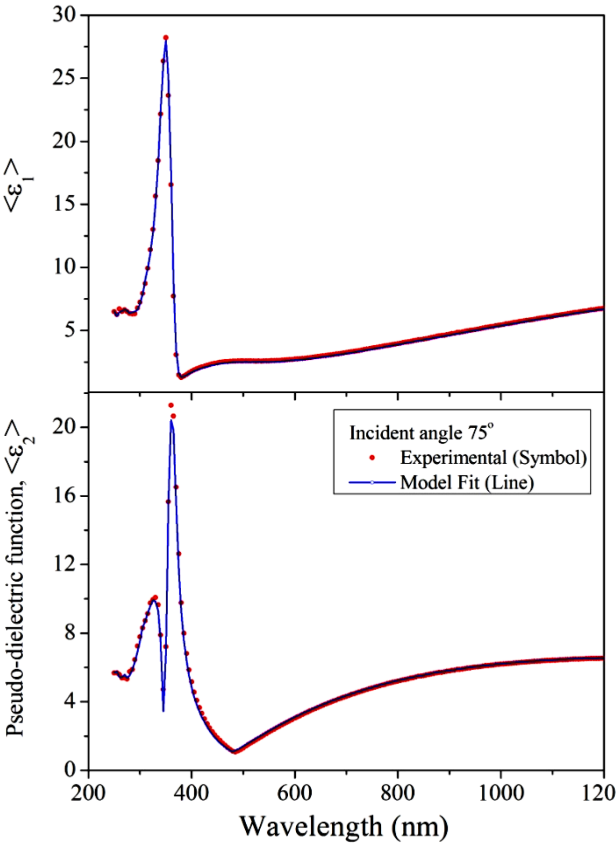

Fig. 4. Real $<\varepsilon_1>$ and imaginary part $<\varepsilon_2>$ of the pseudo-dielectric function spectrum of CeO_2 thin films deposited at 700°C. Solid line indicates model fit.

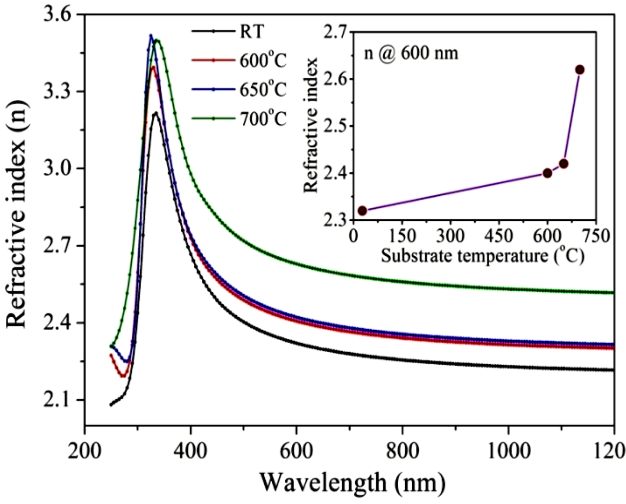

Fig. 5. Dispersion behavior of refractive index (n) of CeO_2 thin films deposited at different substrate temperature. Inset shows the value of n at 600 nm wavelength.

According to inter-band absorption theory, optical band gap of the films can be calculated using the following Tauc relation **[29]**,

$$\alpha h\nu = A(h\nu - E_g)^n$$

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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 α has been extracted from the ellipsometric data after model fitting. Here, the indirect band gap of the CeO_2 films was evaluated by extrapolating the straight line part of the curves $(\alpha h\nu)^{1/2} = 0$ as shown in **Fig. 6**.

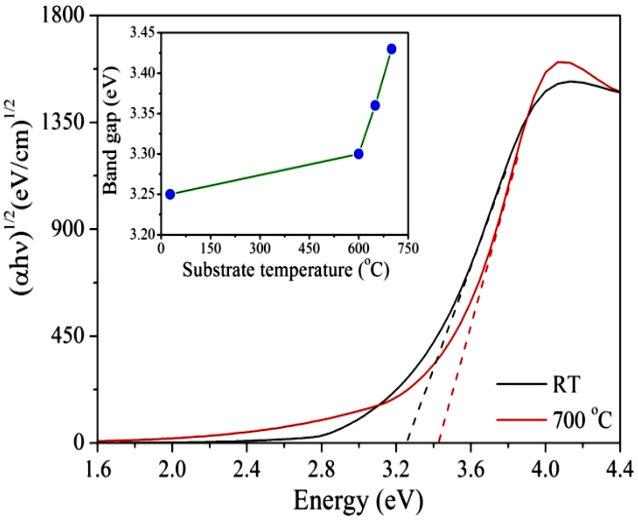

Fig. 6. $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of the CeO_2 thin films deposited at room temperature and 700°C. Inset shows the variation of optical band gap with respect to the substrate temperature.

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 band gap with respect to the substrate temperature. The calculated values of band gap was found to be 3.25, 3.30, 3.36 and 3.43eV for the films deposited at substrate temperature RT, 600, 650 and 700°C, respectively (**Table 1**). We have observed the increase in value of band gap with increasing in substrate temperature which could be due to increase in film density and increase in crystallite size from 6.65 to 21.50 nm (XRD results) and is also in agreement with the reported results **[21, 22, 28]**. Thus, the optical properties of nanocrystalline CeO_2 thin films were found to be strongly influenced by the growth technique and substrate temperature. Wettable properties of nanocrystalline CeO_2 thin films are studied by Contact angle measurement as shown in **Fig. 7**. A surface coating represents hydrophobic nature if the contact angle is $\theta > 90^o$ or hydrophilic in nature if the contact angle is $\theta < 90^o$ **[30]**. It has been observed that the value of contact angle decreased from 122.36° to < 90° when the substrate temperature raised from RT to 700°C as shown in **Table 1**.

The surface roughness of the deposited CeO_2 film may play a role to determine the wettability **[25]**. However, it is unlikely that the very low surface roughness (0.65 ~ 1.15 nm) in our deposited CeO_2 films to cause such a large contact angle difference resulting in the observed transition from hydrophobic to hydrophilic property. As revealed by XRD results, the CeO_2 film gets converted from multi orientation to single orientated film when the substrate temperature increased from RT to ≥ 600°C. This may be the possible reason for the observed hydrophilic nature of high temperature deposited film.

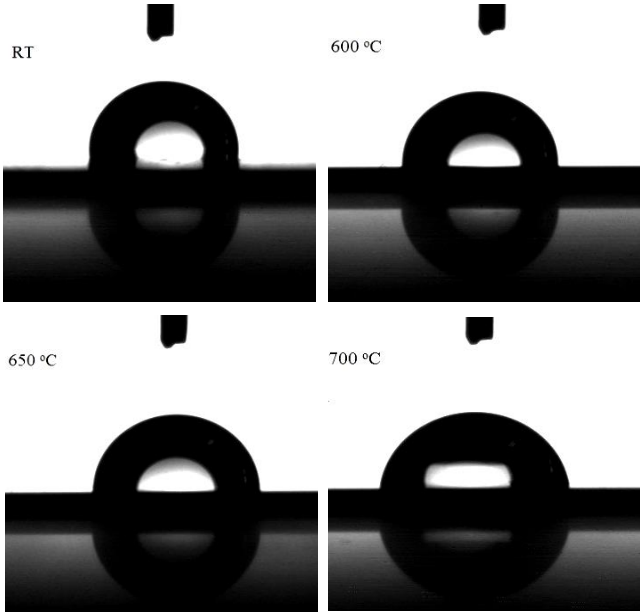

Fig. 7. Contact angle measurement images of CeO_2 thin films deposited at different substrate temperature.

Conclusion

Single oriented nanocrystalline CeO_2 thin films were deposited on Si (100) substrate by RF magnetron sputtering technique at different substrate temperatures. XRD studies of the as deposited CeO_2 thin films at high temperature show predominant (111) orientation. The crystallite size corresponding to (111) peak increased from 6.65 to 21.50 nm with increasing substrate temperature from RT to 700°C. AFM results reveal highly smooth surface with the roughness below 1.15 nm. The maximum refractive index and optical band gap of CeO_2 thin films deposited at 700°C were found to be 2.66 and 3.43 eV, respectively. The wettable properties show a transformation from hydrophobic to hydrophilic in nature with increased the substrate temperature. Thus, these results indicate the possibility of producing nanocrystalline CeO_2 thin films by RF magnetron sputtering with varying properties simply by controlling the substrate temperature for various device applications.

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