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Control of crystal structure, morphology and optical properties of ceria films by post deposition annealing treatments

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ABSTRACT

In this paper, the effects of post-deposition annealing temperature and atmosphere on the properties of pulsed DC magnetron sputtered ceria (CeO_2) thin films, including crystalline structure, grain size and shape and optical properties were investigated. Experimental results, obtained from X-ray diffraction (XRD), showed that the prepared films crystallised predominantly in the CeO_2 cubic fluorite structure, although evidence of Ce_2O_3 was also seen and this was quantified by a Rietveld refinement. The anneal temperature and oxygen content of the Ar/O_2 annealing atmosphere both played important roles on the size and shape of the nanocrystals as determined by atomic force microscopy (AFM). The average grain size (determined by an AFM) as well as the out of plane coherence length (obtained from XRD) varied with increasing oxygen flow rate (OFR) in the annealing chamber. In addition, the shape of the grains seen in the AFM studies transformed from circular to triangular as the OFR was raised from 20 sccm to 30 sccm during an 800 °C thermal anneal. X-ray photoelectron spectroscopy was used to measure near-surface oxidation states of the thin-films with varying OFR in the annealing chamber. The bandgap energies were estimated from the ultra-violet and visible absorption spectra and low-temperature photoluminescence. An extracted bandgap value of 3.04 eV was determined for as-deposited CeO_2 films and this value increased with increasing annealing temperatures. However, no difference was observed in bandgap energies with variation of annealing atmosphere.

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1. Introduction

Cerium oxides (CeO_2) have recently attracted much interest due to their chemical stability and unique chemical and physical properties, which make them suitable for many applications [1]. The valence of the Ce ion is very important in determining the structure of cerium oxides; trivalent Ce forms the sesquioxide Ce_2O_3 , which has a hexagonal lattice ($P\overline{3}\ m1$ space group), while tetravalent Ce forms CeO_2, commonly known as ceria, which has a cubic fluorite lattice (*Fm3m* space group) [2–4]. Thin films of the most common CeO_2 exhibit unique physical properties, such as a lattice constant similar to that of Si ($\alpha = 0.541$ nm), a high refractive index and a high dielectric constant [5,6]. Hence, CeO_2 films are appropriate for many applications in optical devices [7,8], microelectronic devices [9,10], optoelectronic devices [11] and sensors [12]. They can also be utilised in other applications by effectively incorporating porosity between intermediate thin film layers to make thick porous structures. These further application areas include solar–thermal fuel generation [13], industrial catalysis [14,15], solid oxide fuel cells [16] and oxidation prevention of human cells in biomedical devices [17].

Since CeO_2 is stable even in sub-stoichiometric form ($CeO_{2-\delta}$), it has been produced by several growth techniques including electron-beam evaporation [18], chemical vapour deposition [10], ion-beam-assisted deposition [19,20], pulsed laser deposition [21] and reactive and non-reactive magnetron sputtering [6,13]. However, magnetron sputtering is one of the most attractive techniques for the preparation of CeO_2 films due to many advantages associated with the technique, including low substrate temperatures, scalability and good surface roughness characteristics [13], in addition to it being a well-established and relatively low cost industrial technique. Furthermore, the bipolar pulsed DC magnetron sputtering (PDCMS) process has attracted even greater attention recently because it shows higher deposition rates of defect-free ceramic films compared to conventional RF magnetron sputtering processes and therefore has potential as a commercially suitable method for large-area deposition of good quality ceramic films with high yield under diverse processing conditions [13].

According to various reports in the literature, highly crystalline CeO_2 can be obtained by applying heat to the substrate during deposition [22, 23]. However, this can also be achieved by post-deposition annealing of

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the CeO_2 film at high temperatures. Varying the substrate temperature during growth has an effect on the structural, chemical and optical properties but these effects are different to those obtained from varying oxygen flow rates (OFRs) during post-deposition annealing, especially in terms of microstructure (grain size and shape) of the films. Varying the post-deposition annealing temperature or the OFRs also results in changes in the concentration of oxygen vacancies, due to the altered thermodynamic equilibrium [24]. These factors can also influence the structure and morphology of CeO_2 films [25–27], which play an important role in solid/solid catalysis and the electrical properties of CeO_2 [28, 29] Thus varying OFRs and temperature during post-deposition annealing offers potential for control and engineering of a thin film properties.

In this work, we characterise CeO_2 thin films grown on Si(100) and quartz substrates grown by PDCMS using a CeO_2 target. The influence of varying the OFR and post-deposition annealing temperature on the deposit characteristics (microstructure and morphology, composition, optical properties etc.) was studied. The films were analysed by X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible (UV–Vis) spectroscopy and low-temperature photoluminescence (LPL). The influence of the post-deposition anneal temperature and variation of the OFRs on the PDCMS CeO_2 film properties have not been reported previously, and our work provides useful information on the effects of temperature and variation of OFRs in terms of controlling thin film properties, specifically grain shape and size.

2. Experimental

2.1. Material synthesis

Nanostructured CeO_2 thin films were prepared by PDCMS of a CeO_2 target onto silicon and quartz substrates (2 × 2 cm). The target was 99.99% pure cerium oxide (50 mm diameter and 6 mm thickness, supplied by the Kurt J. Lesker Company). Prior to deposition, the substrates were ultrasonically cleaned using acetone, a decontamination solution (30905 Aldrich), de-ionised water and blown dry with a nitrogen stream. An ENI RPG-100 pulse generator was used to drive a planar magnetron fitted with the CeO_2 target in power regulation mode. The chamber was first pumped down to a base pressure of 2×10^{-5} Pa by cryogenic pumping. The target was pre-sputtered for 10 min prior to deposition to reduce target surface contamination and to obtain a stable plasma density. Sputtering was carried out in a pure Ar atmosphere and the working pressure was adjusted and maintained at 0.7 Pa for the duration of the deposition. The target to substrate distance was adjusted to 6 cm. The sputtering was done at room temperature using a power of 65 W at 150 kHz without intentional heating. The substrates were at floating potential and the sputtering time was adjusted to 60 min to obtain a uniform film thickness of 50 ± 10 nm for all the deposited samples.

2.2. Annealing

After deposition and a short contact time with air at room temperature, the CeO_2 thin films samples were transferred into a quartz glass cell, where annealing treatments were performed. Samples were ramped up to target temperatures of 500 °C, 800 °C and 1000 °C at a rate (r) of 40 °C min^{-1} in an air ambient, and held at these temperatures for 1 h (the dwell time, t_d), in order to study the effect of annealing temperature on the film properties. An optimum temperature of 800 °C ($r = 40$ °C min^{-1}, $t_d = 1$ h) was chosen and further annealing experiments were carried out to study the effect of varying the oxygen partial pressure ($p(O_2)$) during annealing on the PDCMS deposited CeO_2 films. This was done by heating CeO_2 thin films deposits in an Ar/O_2 atmosphere with various OFR values at 800 °C, while keeping the argon flow rate (AFR) constant. The OFRs were varied in the range 0–50 sccm. After 1 h of annealing, the sample was allowed to cool down to room temperature (cooling time ≈ 30 min) before characterisation. Note that before each new annealing step, the gas atmosphere was refreshing by pumping and refilling.

2.3. Structure and morphology

The structural properties of the sputtered CeO_2 films were measured using a Bruker D8 advance X-ray diffractometer with CuK_α radiation of wavelength $\lambda = 1.54056$ Å to determine the crystallinity of the films. The XRD measurements were carried out in locked-coupled ($\theta - 2\theta$) mode in a 2θ range from 20° to 60°. A qualitative and quantitative phase analysis of the different phases was done by Rietveld analysis of the diffraction data using the FullProf program [30].

The surface morphology and roughness of the CeO_2 films were studied by a Veeco Nanoscope Dimension 3100 AFM instrument operating in tapping mode using aluminium-coated silicon (Si) probes (Budget Sensors, Tap300Al-G) with a tip radius of <10 nm. The intrinsic height resolution of the system is determined by the piezoelectric element and electronic noise and is ~0.4 nm, which provides a base level for measurement reliability. The surface roughness of each sample was determined as the root mean square (RMS) value R_q of the distribution of heights in the AFM topography images. The row/column statistical tool of Gwyddion software was used to calculate the standard deviation of R_q of all individual row/column values, and the values obtained were considered when determining the roughness error bars [31]. Where the calculated standard deviation of all individual row/column values is greater than the intrinsic height resolution of the system, the standard deviation is used as the error bar, and where it is less than the intrinsic height resolution, a value of 0.4 nm is used as the error bar.

2.4. Spectroscopy

XPS analysis was carried out using a VG Microtech electron spectrometer with a base pressure of 1×10^{-7} Pa. The photoelectrons were excited with a conventional Mg K_α ($h\nu = 1253.6$ eV) X-ray source and an electron energy analyser operating at a 20 eV pass energy, yielding an overall resolution of 1.2 eV. The samples were subjected to a mild degassing procedure in UHV at 300 °C in order to eliminate any surface contamination (this treatment was at too low a temperature to affect the properties being studied as a function of post deposition annealing), which may have arisen as a result of the transfer in atmosphere between the deposition and analysis chambers.

The optical absorption properties of the CeO_2 films were studied at room temperature using a Perkin Elmer Lambda 40 UV–Vis spectrometer in the range from 400 to 800 nm with a resolution of 4 nm. LPL measurements were carried out from 10 K to 22 K using a closed cycle helium cryostat system and a 325 nm excitation (He–Cd laser). The luminescence was analysed using a 1 m grating spectrometer (SPEX 1704) with a photomultiplier tube (Hamamatsu model R3310-02) in photon counting mode and cooled to −20 °C by a Peltier cooler (EMI FACT50).

3. Results & discussions

3.1. Structure and morphology

Fig. 1 shows a series of XRD θ–2θ patterns from the CeO_2 thin films: as-deposited and post-deposition annealed at temperatures of 500 °C, 800 °C and 1000 °C for 1 h in an air ambient. As seen in Fig. 1, the as-deposited CeO_2 films show a broad and featureless XRD pattern, characteristic of an amorphous structure. The CeO_2 films annealed at 500 °C shows the emergence of prominent diffraction peaks indexed to the cubic fluorite CeO_2 structure (PDF No. 00-034-0394), revealing that the CeO_2 films are being crystallized by the annealing process. For the films annealed at 800 °C and 1000 °C, we observe a higher intensity for the CeO_2 diffraction peaks which clearly reveals that the crystalline

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