Spray pyrolysis for the production of biaxially textured MgO thin films for second generation coated conductors

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DOI:
10.1088/1742-6596/97/1/012098

Journal of Physics: Conference Series **97** (2008) 012098 doi:10.1088/1742-6596/97/1/012098

Effort to Produce Textured CeO_2 and MgO Films by the Spray Pyrolysis Technique as Buffer Layers for Coated Conductors

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Abstract. The possibility of using spray pyrolysis as a simple, chemical, low cost method for the production of CeO_2 and MgO thin films widely used as buffer layers for second generation coated conductors was examined. CeO_2 films were produced on borosilicate glass substrates and four different surface morphologies were observed at different deposition temperatures. The smoothest films were obtained when the process was described as low temperature chemical vapour deposition. In addition, c-axis textured CeO_2 films have been deposited on Si (100) single crystal, but the surface morphology was quite rough, consisting of distinct particles indicating that further optimisation is needed. On the other hand c-axis textured MgO films with smooth morphologies were deposited on Si (100) single crystal. Rocking curves revealed an excellent out of plane texture with a FWHM between 0.95^0 and 1.01^0

1. Introduction

The spray pyrolysis method presents numerous advantages such as simplicity, low cost, non toxic precursors, good reproducibility, and no need for vacuum; it has been therefore used over the years for the production of thin films of simple oxides, mixed oxides, metallic spinel type oxides, chalcogenides films [1].

One of the problems for the commercialisation of the coated conductors is the high cost related to the expensive physical methods employed for the fabrication of the YBCO superconducting material and the essential buffer layers [2]. Recently low cost chemical routes such as MOD have been employed to substitute the complex physical methods [3] [4]. Despite spray pyrolysis being one of the most well known low cost chemical deposition method for thin films, it has non been widely used for the production of either the superconducting layers or the buffer layers for coated conductor architectures.

There are few reports referring to the production of YBCO films by the aforementioned method [5] [6]. Previously, Shields et al have reported the production of YBCO films on STO (100) single crystal substrates [7]. The precursor solutions have been prepared by dissolving Y_2O_3 $BaCO_3$ and CuO in a mixture of nitric acid and distilled water. Good epitaxial films were produced with a J_c of around $1.9*10^5$ A cm^{-2} (77K, 0 Tesla). Furthermore, YBCO has been deposited on buffered Ni using the same spray parameters identified for the successful deposition of YBCO on STO single crystals [8]. The Ni substrates have been prebuffered with CeO_2/YSZ/CeO_2 layers deposited by pulsed laser deposition.

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CeO_2 has been extensively used as buffer or cap layer in architectures [9] [10]. There are some studies referring to the production of CeO_2 on various substrates by the spray pyrolysis technique but none of these studies concentrate on evaluating the texture of the produced films [11] [12] [13]. Wei et al [14] conducted the most important study in this field. They used a method similar to spray pyrolysis, called electrostatic spray-assisted vapour deposition (ESAVD). Soda lime glass and Si(100) were used in the first place as substrates. CeO_2 thin films deposited on Si (100) are crystallised in the cubic structure with a preferred orientation along the [100] direction. Better alignment is achieved by increasing the electric field. Furthermore, CeO_2 has been deposited on biaxially textured Ni substrates [15]. Once more much smoother films were obtained when higher voltage was applied. The (200) pole figures shows a strong out of plane texture, while the (111) pole figure indicates that an epitaxial relationship of $[110]_{CeO2}$// $[100]_{Ni}$ has been achieved; the four CeO_2 (111) poles located at about 45° rotation from Ni (111) poles.

MgO thin films have been widely used as buffer or template layers for YBCO coated conductor architectures [16] [17]. MgO has been deposited on various substrates by spray pyrolysis but once again the texture of the obtained films is not the main focus of these studies [18] [19] [20] [21]. The main focus in this paper will be to produce CeO_2 and MgO thin films, widely used as buffer layers in the coated conductor architectures.

2. Experimental details

The experimental set up has been described in detail elsewhere [22]. Briefly, the atomization of the initial chemical solution was achieved with the help of a commercial ultrasonic nebuliser (OMRON, model NE-U17). The substrate was attached to a stainless steel holder, which was positioned in the middle of the cylindrical furnace (height 30 cm, diameter 15 cm). Argon gas was used to transport the mist produced in the nebuliser onto the substrate. During spraying the temperature of the substrate was observed to drop 5-7^{0}C for each 15 s spray. After 15 s, therefore, the gas flow was turned off for 1 min and 45 s and the substrate was allowed to stabilize to its set temperature. The solutions were prepared by dissolving an appropriate amount of $Ce(NO_3)_3.6H_2O$ and $Mg(NO_3)_2.6H_2O$ in 100 ml of distilled water for the production of CeO_2 and MgO thin films respectively.

The structural properties of the films were studied by the XRD theta- 2 theta technique and rocking curves with the aid of a 2-circle Siemens diffractometer. Surface morphology and fracture cross section thickness were examined in a JEOL 7000 SEM and surface roughness by contact mode AFM (Dimension 3100).

3. Results and discussion

3.1. Preparation of CeO_2 Thin films

3.1.1. CeO_2 on borosilicate glass

The effect of some of the most important deposition parameters (temperature, solution concentration, flow rate, deposition time, cooling rate) on the structure and the morphology of CeO_2 thin films were examined with the aim to obtain some understanding of the mechanisms involved in the spray pyrolysis deposition. It was identified that the substrate temperature is the deposition parameter that has the most effect on the properties of the produced films. In this study we will concentrate on films deposited from 0.0461 M solutions with the flow rate equal to 10 litres/min and the deposition time set to 32 min. The deposition temperature was varied between 200-600° C.

For the film deposited at 200^{0}C none of the x-ray peaks observed corresponds to CeO_2; the nitrates used for the deposition have not been decomposed and therefore higher substrate temperatures should be employed. The XRD pattern of the film prepared at 250^{0}C starts to show some weak peaks corresponding to CeO_2 (Figure 1). For films deposited at higher temperatures these peaks are becoming more pronounced. For the films deposited at 250^{0}C, 350^{0}C the peak that corresponds to the

(111) plane is the most intense while at higher temperatures (450^0-600^0C) the (200) peak becomes the strongest.

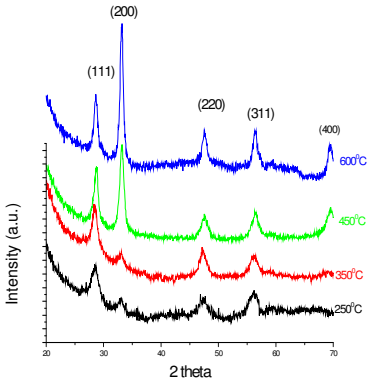

Figure 1: XRD patterns of CeO_2 films deposited on borosilicate glass from 0.0461M solutions at various temeratures.

Three different morphologies are detected according to the temperature used: a) at low temperatures (250^0-300^0C) extremely rough films are obtained with a spaghetti-like morphology (Figure 2), b) at medium temperatures (350-550°C) smoother films are obtained- the smoothest morphology is detected for the film deposited at 350°C (Figure 3), c) at higher temperatures (600^0C) the film surface is quite rough since it consists of distinct particles with sizes varying from 1μm to 3μm (Figure 4) .

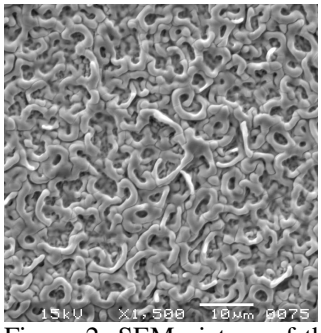

Figure 2: SEM picture of the CeO_2 film deposited on borosilicate glass at 250℃ from a 0.0461 M solution.

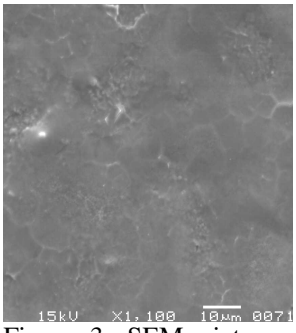

Figure 3: SEM picture of the CeO_2 film deposited on borosilicate glass at 350°C from a 0.0461 M solution.

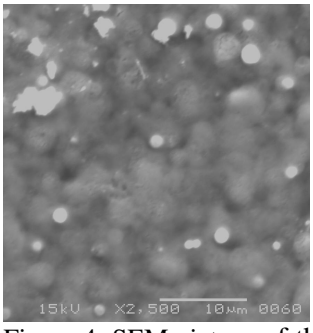

Figure 4: SEM picture of the CeO2 film deposited on borosilicate glass at 600℃ from a 0.0461 M solution.

G. Blandenet et al [23] suggested four possible growth modes for the spray pyrolysis process as a function of the temperature that can be correlated with the observed morphology in our case according to the following: At temperatures < 250^0C the droplet impinges on the substrate where evaporation takes place. This can explain the obtained XRD pattern of the film deposited at 200^0C where none of the observed peaks correspond to cubic ceria, indicating that full decomposition of the nitrates has not taken place. At temperatures between 250^0 and 300^0C the evaporation of the solvent is complete just prior to contacting the substrate, followed by the decomposition of the nitrates to oxides. In the temperature range between 350^0-550^0C the growth mode can be characterized as low temperature chemical vapour deposition (CVD) since it involves volatilisation of the dried metal salt, diffusion of the vapour to the substrate, followed by decomposition to the oxide. When the temperature is around 350^0C films are quite smooth indicating that this is the optimum temperature. Many authors propose

that the smoothest films are deposited when they are produced at the low temperature CVD regime [21] [24] [25]. Lastly at temperatures > 550^0C the morphology consists of distinct particles indicating that the oxide particles are formed well above the substrate.

More details about the effect of the different deposition parameters on the properties of the produced films and comments about the correlation between the preferred orientations of the films with the observed morphology can be found elsewhere [22].

3.1.2. CeO_2 on Si (100) single crystals

The next step involved the efforts to epitaxially grow CeO_2 thin films on single crystals with the aim to produce biaxially textured films that can be used as buffer layers in second generation coated conductors. Si (100) is used as a single crystal since its lattice mismatch with CeO_2 is quite small around 0.40 %.

Figure 5 presents the XRD pattern of the CeO_2 deposited at 550° C from a 0.0461 M solution (the flow rate was set to 10 l/min while the deposition time was fixed to 32 min). It is observed that the (200) peak is the strongest indicating that the produced film are c-axis preferentially oriented. On the other hand the (111), (222) and (311) peaks are also detected. The morphology of the film consists of distinct particles indicating that the oxide particles are formed well above the substrate (Figure 6). This is a typical morphology when we operate under the fourth growth mode that has been described earlier. However, the smoothest films are obtained when the process can be described as low temperature CVD. A further optimisation is therefore needed with the scope to function at the CVD regime. Similar results have been obtained by the ESAVD method [14]. Better alignment and smoother films were obtained simply by increasing the electric field.

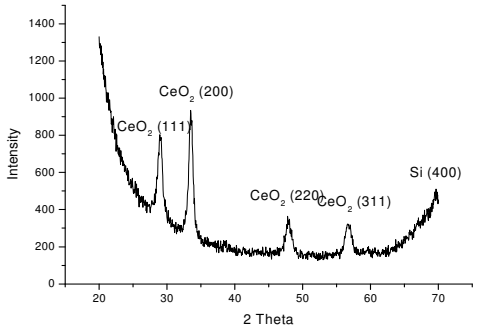

Figure 5: XRD pattern of the CeO_2 film deposited on Si (100) at 550^0C from a 0.0461 M solution

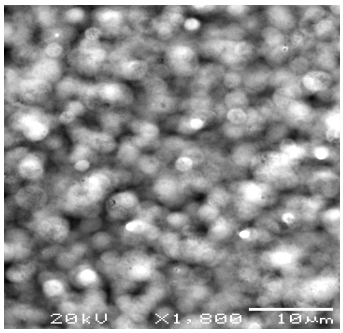

Figure 6: SEM picture of the CeO_2 film deposited on Si (100) at 550^0C from a 0.0461 M solution

3.2. Preparation of MgO thin films

In this section we will concentrate on the efforts to produce biaxially textured MgO thin films by depositing them on Si (100) single crystal substrates. In this case the lattice mismatch is 28.8 % but if the MgO unit cell rotates by 45° the lattice mismatch is equal to 9.7 %.

Figure 7 illustrates the XRD pattern obtained from the film deposited at 650°C from a 0.078 M solution- the deposition time was set to 64 min and the flow rate was fixed to 10 l/min. The films are c-axis oriented since only the peaks from the Si substrate and the MgO (200) plane are detected. The peaks noted as * can be attributed to high order reflections from the substrate. The rocking curve of the (200) peak of the deposited film shows a FWHM equal to 0.95^0 indicating that the produced film presented an excellent out of plane texture (Figure 8). The rms roughness calculated from the 3-D 5*5 μm^2 AFM picture is 43.3 nm (Figure 9). SEM studies of the cross section of the fractured surface (Figure 10) illustrate a dense and homogeneous MgO layer with film thickness estimated between 1650 to 1750 nm.

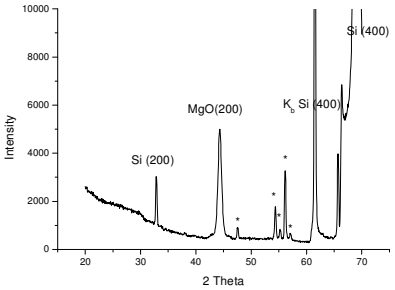

Figure 7: XRD pattern of the MgO film deposited on Si (100) at 650°C from a 0.078 M solution

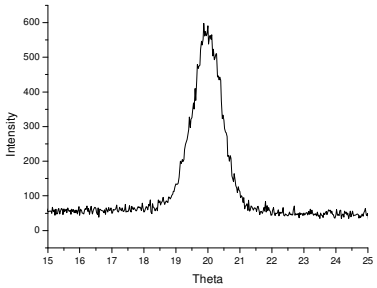

Figure 8: Rocking curve of the MgO (200) peak of the MgO film deposited on Si (100) at 650°C from a 0.078 M solution

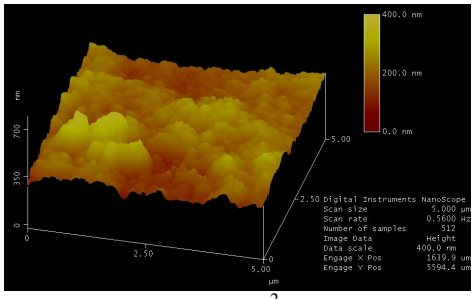

Figure 9: 3-D 5*5 μm^2 AFM picture of the MgO film deposited on Si (100) at 650°C from a 0.078 M solution with a deposition time equal to 64 min

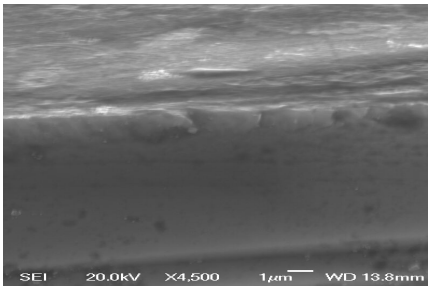

Figure 10: SEM picture of the fracture cross section of the MgO film deposited on Si (100) at 650°C from a 0.078 M solution with a deposition time equal to 64 min

Films with reduced thickness were obtained when the deposition time was reduced to 32 min- temperature, solution concentration and flow rate were kept constant. The thickness of the film is between 650 to 750 nm. The produced film is once more c-axis textured as identified from the XRD pattern. The FWHM as calculated from the rocking curve is 1.01°. The rms roughness as calculated from the 3D AFM picture in a 5*5 μm^2 area is 22.6 nm (Figure 11).

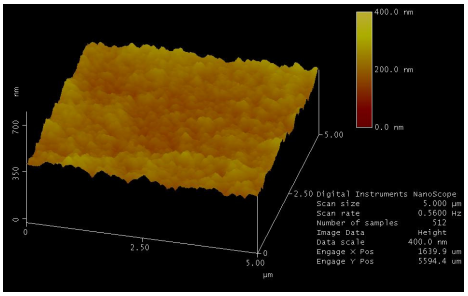

Figure 11: 3-D 5*5 μm^2 AFM image of the MgO film deposited on Si (100) at 650°C from a 0.078 M solution with a deposition time equal to 32 min

4. Conclusion

The four different surface morphologies were observed for CeO_2 films deposited on borosilicate glass, which could be associated with four typical growth modes for the spray pyrolysis method. The smoothest films were obtained when the temperature was 350^{0}C such as the process could be

described as low temperature CVD. C-axis preferred oriented CeO_2 were deposited on Si (100) single crystal. However, further optimisation is needed since the surface morphology was quite rough.

C-axis textured MgO films with various deposition times were obtained on Si (100) single crystal. As the overall deposition time was increased from 32 min to 64 min, the thickness and the rms roughness of the produced film was approximately doubled indicating that a good control over the process was acquired. All the films exhibited an excellent out of plane texture with a FWHM varying from 0.95^0 to 1.01^0.

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