Large-area production of yttria-stabilized zirconia by pulsed laser deposition

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Abstract. The small size of most of the present-day films produced by PLD (up to few cm2) is not only a general limiting factor for applications in many scientific and technical fields, but is also problematic for studies of samples for which edge effects may play an important role. Yttria-stabilized zirconia (YSZ) films with a uniform thickness have been deposited at different distances from the target and at different oxygen background pressure in the large-area PLD facility at Risø National Laboratory. Films of uniform thickness up to 300 nm and 1200 nm over an area with a diameter of more than 90 mm were achieved. Depending on the oxygen background pressure the YSZ films were found to grow in a highly oriented manner on the Si wafer.

1. Introduction

One goal in the development of solid oxide fuel cells (SOFC) is a lowering of the operating temperature. Amongst other things, this will require thin electrolytes and/or new electrolyte materials. The electrolyte must be thin and dense (gas tight) over large areas. A thin layer of yttria stabilized-zirconia oxide (YSZ) has been demonstrated being a good ionic conductor and at the same time being highly resistant to electron transport.

A particular configuration of a large-area PLD Facility has recently been installed at Risø National Laboratory. The advantage of PLD is that the stoichiometry of the target can be transferred to a film even for targets of complicated chemical composition [1-3]. Using this facility it is now possible to deposit layers with high uniformity over an area that exceeds 50-100 cm². However, a quantitative and non-destructive determination of the thickness is needed, and we have, therefore, developed a new non-destructive method [4]. With this method no film standards are required, and the thickness of any elemental film on any substrate size can be determined from theoretical calibration curves. In the present paper we report the effect of process parameters such as oxygen partial pressure and target-substrate distance on the film uniformity and on the stoichiometry of YSZ films.

2. Experiments

A target of YSZ was irradiated with 20-ns laser pulses from an excimer laser at 248 nm with a fluence of 2 J/cm² [4]. The process parameters were optimized with respect to film thickness homogeneity by varying the repetition rate and the corresponding deposition time at each location along the target. The
ablated material was collected on a substrate located at a distance of 80 mm or 65 mm from the target. The films were deposited on a 100-mm Si (111) wafer. During the deposition, which lasts 120 minutes, the substrate temperature was kept constant at a selected value of 700°C with an oxygen background gas of 0.05, 0.1 and 0.2 mbar. The YSZ target with a diameter of 76 mm and a thickness of 6 mm was characterized structurally as cubic YSZ (space group: Fm-3m) using a diffractometer with a Cu-Kα. The YSZ film thickness over the full film area is determined by energy-dispersive x-ray spectrometry in a scanning electron microscope (SEM) and compared with Monte Carlo simulations for various values of the film thickness. The examination of all samples was carried out using a Low Vacuum Scanning Electron Microscope (LVSEM) with a beam voltage of 20 kV. A detailed description of the method is reported elsewhere [4].

3. Results and discussions
3.1. Film thickness
The maximum thickness of the films is found to range from 300 to 1200 nm depending on the oxygen partial pressure and the target to substrate distance. All films show dense and crack-free coatings with a uniform thickness over a major part of the 100 mm Si wafers. Regardless of the target-substrate distance, the deposition rate is found to decrease with increasing oxygen pressure as a result of the increasing scattering of the target atoms by the oxygen molecules, as also reported elsewhere [5]. Figure 1 shows the measured film thickness for different oxygen pressure and different target-substrate distances. As seen from these figures the overall thickness of the films seems to increase by changing the target-to-substrate distance, e.g. from 65 mm to 80 mm.

This surprising result cannot easily be explained, since the angular distribution of the arriving ablated material broadens and the magnitude of the arriving flow decreases with increasing pressure [5]. However, it is also known that in the initial stage of the plume development highly energetic ions are formed [6] which may cause sputtering of the growing film. The slowing down of the plume atoms and molecules is much more pronounced for a larger substrate-target distance, and the sputtering rate of the film will be significantly smaller. The results also indicate that there is probably a certain optimum value of distance, for which the kinetic energy of the ablated atoms and molecules at the film surface is below the threshold for sputtering and damage, but where the flow not yet is significantly reduced due to the large substrate-target distance.

Figure 1. The thickness profile of a 100-mm Si wafer coated with YSZ. (a) substrate-target distance of 80 mm and different oxygen partial pressure, 0.05, 0.1 and 0.2 mbar, (b) substrate-target distance of 65 mm and different oxygen partial pressure, 0.05, 0.1 and 0.2 mbar.
The maximum of the measured thickness value as a function of the oxygen background pressure is shown in Figure (2). As seen from this figure, the maximum film thickness is significantly larger for the distance of 80 mm than for that of 65 mm.

Figure 2 Maximum film thickness as a function of oxygen background pressure. The lines are linear fits.

3.2. Structural determination
Fig. 3 shows the XRD pattern of the film deposited on Si(111) substrate for a background pressure of 0.05, 0.1 and 0.2 mbar for substrate-target distances of 80 and 65 mm together with the theoretical pattern of YSZ. The peak positions of the deposited film correspond well to the cubic type YSZ. The good correspondence indicates that the stoichiometry of the target is essentially similar to that of the target.

Figure 3 (a) XRD pattern of a YSZ thin film on a Si (111) substrate at a substrate-target distance of 80 mm. The theoretical pattern of YSZ is also shown, (b) XRD pattern of YSZ thin film on Si (111) substrate at a substrate-target distance of 65 mm.

As seen from Figure 3(a) and (b) the YSZ films show a significant YSZ(200) orientation for oxygen background pressure of 0.05 and 0.1 mbar. Investigations of the full width at half maximum (FWHM) of the (200) ω-rocking curve of the YSZ found to be about 0.6° for the samples deposited at 0.05 and 0.1 mbar indicate high crystallinity of the film as also observed by [10]. At first sight the results imply that the epitaxial relationship between the YSZ layer and Si substrate is cube-on-cube with YSZ(000) // Si(111). However, further investigations have shown that YSZ deposited on different substrates types grow with a certain preferred orientation, i.e. YSZ(00), regardless the orientation of the substrate. The results of these investigations will be published in a separate publication. The
observed orientation YSZ(00) has previously been reported to exist for various deposition techniques independent of the substrate type; flow-type hot-wall Atomic Layer Epitaxy (ALE) [7] in which YSZ was deposited on Si (100) substrate, CVD [8] where YZS was coated onto a Silver (100) substrate and DC sputtering [9] with deposition of YSZ on a Ni (111) substrate. For an oxygen background pressure higher than 0.1 mbar it seems that the films grow without or at least with less preferred orientation indicating that the partial pressure of oxygen evidently does play a role in the formation of oriented yttria-stabilized zirconia compounds. We also note that YSZ films deposited at room temperature does not show this growth direction [11].

4. Conclusions
We have investigated the effect of substrate-target distance as well as the pressure effect on the growth of YSZ on a large Si wafer of 100 mm. Films of uniform thickness of over an area with a diameter of more than 90 mm were achieved. The thickness of the films was found to depend on the oxygen pressure and decrease with increasing oxygen background pressure. Depending on the oxygen background pressure the growth of the YSZ is found to be oriented with the growth direction YSZ[00]//Si[111].

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