Epitaxial growth of Y-doped $SrZrO_3$ films on MgO by pulsed laser deposition

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Epitaxial thin films of Y-doped $SrZrO_3$ have been grown on MgO(001) by pulsed laser deposition. The deposition process has been performed at temperatures of 1000–1200 °C and at an oxygen pressure of 1.5×10^{-1} mbar. The samples are characterized by Rutherford backscattering spectrometry/channeling (RBS/C) and x-ray diffraction (XRD). We found an epitaxial relationship of $SrZrO_3$ $(0k0)$ [101]‖MgO (001) [100]. Good crystalline quality is confirmed by RBS/C minimum yield values of 9% and a FWHM of 0.35° of the XRD rocking curve. © *1996 American Institute of Physics.* [S0021-8979(96)09705-1]

Presently high-temperature protonic conductors are receiving increasing attention because of their applications in fuel cells, electrolyzers, and gas sensors. It is known that hydrogen is solvable in various oxides. In 1981 Iwahara *et al.*[1] found that some perovskite-type oxides such as $SrCeO_3$ and $BaCeO_3$ exhibit considerable proton conduction after replacing a fraction of the Ce^{4+} ions by Yb^{3+}. The search for new protonic conductors with increased chemical and mechanical stability led to zirconates such as $CaZrO_3$ (Ref. 2) and $SrZrO_3$ (Ref. 3). In this publication we focus on the latter material.

Up to now, the majority of reports about $SrZrO_3$ deal with polycrystalline material prepared by conventional ceramic techniques. However, for exact materials science high quality crystals are desirable. Consequently Y-doped $SrZrO_3$ has been synthesized in single crystalline form, utilizing the float zone process,[3] and its protonic conduction has been demonstrated.[4] Since this approach is very difficult, there is a demand for alternate processes. Particularly thin film technology might solve this problem, if high-quality epitaxial thin films can be produced. Recently, there were reports of successful thin film growth of $BaCeO_3$ by using metalorganic chemical vapor deposition (MOCVD)[5] and rf sputtering.[6] Both methods produce single phase films. In the case of rf sputtering they are strongly textured, but not epitaxial. Our aim is to use pulsed laser deposition (PLD)[7] as another thin film technique to produce epitaxial films in various thicknesses.

Since the advent of high-temperature superconducting (HTS) oxides and the fabrication of very high quality HTS thin films, PLD established itself as a successful tool for thin film processing. The PLD systems are simple, flexible, and not as expensive as some of the other thin film deposition tools. The advantages of this process include the well-defined and stoichiometric deposition even of compound targets and the short process times due to high growth rates. The deposition in a reactive atmosphere such as oxygen offers specific benefits for multicomponent oxides. In this publication we demonstrate the high potential of PLD for the growth of perovskite-type protonic conductors such as $SrZrO_3$.

MgO is a suitable substrate for epitaxial films of $SrZrO_3$. Its crystalline structure is cubic with an axis length of $a=4.213$ Å.[8] Table I lists the lattice constants of the orthorhombic structure of $SrZrO_3$ and compares it with special directions of the MgO substrate. The lattice mismatch is moderate with values of 2–3%. Other advantages of MgO are its wide window of optical transparency and its stable structure.

The PLD setup for $SrZrO_3$ deposition includes a KrF excimer laser (248 nm, 40 ns, 10 Hz, 2–4 J/cm^2) and has been described in detail elsewhere.[9] The cylindrical target consists of single phase Y:$SrZrO_3$ powder which has been sintered at 1650 °C for 20 h and pressed at 350 MPa. Starting materials were ZrO_2, $SrCO_3$, and Y_2O_3. Note that the ZrO_2 had approx. 1% contamination of HfO_2. The materials were calcined at 1200 °C for 12 h, milled to grains <3 mm, calcined again, milled again, and finally pressed at 350 MPa. The MgO(001) substrates had dimensions of 10×10 mm^2, 1 mm thick. They were placed on a resistive SiC heater in the PLD chamber. The deposition process takes place at an oxygen partial pressure of 1.5×10^{-1} mbar. To improve the stoichiometry, an *in situ* annealing step was included. Directly after completing the deposition process, the chamber was flooded with oxygen and the sample was annealed for 3 min in 1000 mbar oxygen. The SiC heater provided temperatures during deposition and annealing of up to 1200 °C. Typical deposition rates were 1 nm/s. The $SrZrO_3$ films are optically very clear. Sample characterization was performed by Rutherford backscattering spectrometry/channeling (RBS/C) to determine chemical composition, thickness, and crystalline quality of the films. In addition, conventional x-ray diffraction (XRD) was used to analyze the epitaxial orientation of the films.

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TABLE I. Lattice constants of $SrZrO_3$ (Ref. 10), selected suitable lattice constant values of MgO (Ref. 8) and the resulting lattice mismatch for epitaxy of $SrZrO_3$ on MgO.

d ($SrZrO_3$)		d (MgO)		$\Delta d/d$ (MgO)
a [100]	5.814 Å	$\sqrt{2}a\langle 110\rangle$	5.958 Å	2.4%
b [010]	8.196 Å	$2a\langle 200\rangle$	8.426 Å	2.7%
c [001]	5.792 Å	$\sqrt{2}a\langle 110\rangle$	5.958 Å	2.8%

Figure 1 shows the RBS/C spectra of a $SrZrO_3$ film after deposition and subsequent annealing, both at approx. 1100 °C. The energy of the incident He beam was 1.4 MeV. The spectrum is dominated by the Sr and Zr signals from the deposited film. The RUMP computer code was used to simulate the random signal. The result of the simulation is denoted by the dashed line. It verifies the composition of $SrY_{0.05}Zr_{0.935}Hf_{0.015}O_3$ and a layer thickness of 490 nm. This composition corresponds within the experimental errors to the initial target composition. The deviation of the random and simulated spectra at channels lower than 400 stems from inaccurate fitting parameters of the simulation at lower energies. Compared to the spectrum taken in random direction, the aligned crystal shows a strong decrease in backscattered yield, indicating good crystalline quality. The surface peak at channel 800 implies a well-ordered surface. Behind the surface peak, at channels 780–790, the minimum yield is 9%, corresponding to a highly single crystalline $SrZrO_3$ film. Towards lower channel numbers, the aligned signal increases stronger than the random signal, probably due to defects in the deposited film.

Figure 2 shows the $\theta/2\theta$ XRD pattern of a film. RBS/C revealed a film thickness of 450 nm and a minimum yield of 10%. The $\theta/2\theta$ scan shows very narrow reflections of the MgO(001) and the $SrZrO_3$ $(0k0)$ planes. It can be concluded that the film is strongly $(0k0)$ textured, without any other orientations or phases. The full width at half maximum (FWHM) of the rocking curve of the $SrZrO_3$(040) peak is $\Delta\omega = 0.36$, again indicating a high crystalline quality. The

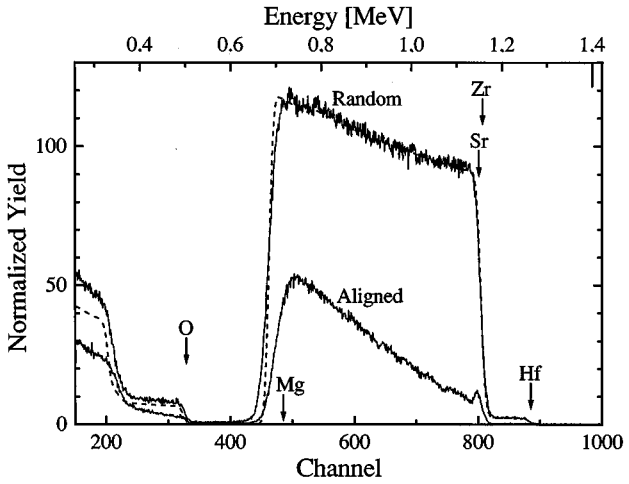

FIG. 1. RBS/C spectra obtained using random and aligned configuration for a $SrZrO_3$ film on MgO. The spectra have been simulated (dashed line) for a film thickness of 490 nm. Incident He ion energy was 1.4 MeV.

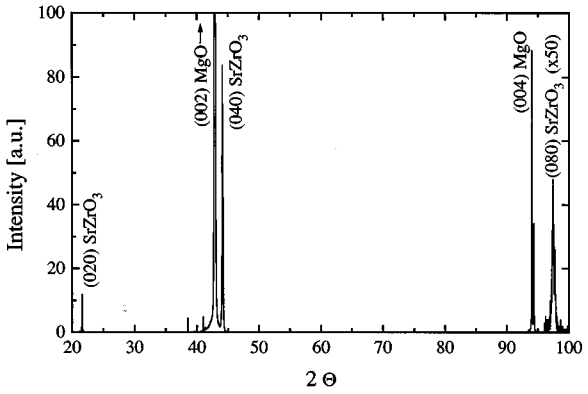

FIG. 2. $\theta/2\theta$ x-ray scan of a 450-nm-thick $SrZrO_3$ film on MgO(001). This scan demonstrates that the $SrZrO_3(0k0)$ planes are parallel to the MgO(001) planes.

in-plane orientation has been investigated by means of Φ scans. The Φ scans of the $SrZrO_3$(165) reflections are plotted in Fig. 3. Two sets of peaks can be observed in the scan of the film, with shifts of 33.7° and 56.3° in relation to the peaks of the MgO Φ scan. The existence of these two sets of peaks is not due to two different in-plane orientations. $SrZrO_3$ grows in the orthorhombic structure, but the a and c axes are very similar, the difference being only 0.4%. Therefore the material is nearly tetragonal. The experimental conditions to realize the Φ scan of $SrZrO_3$(165) and $SrZrO_3$(561) reflections are the same as a result of that (θ values differ by less than 0.1°). In the pattern of Fig. 3 the first set of peaks corresponds to $SrZrO_3$(561) and the second one to $SrZrO_3$(165). The angles of $SrZrO_3$(561) and $SrZrO_3$(165) with MgO(420) in the $(0k0)$ projection are 11.3° and 78.7°, respectively. From these data and the positions of the peaks in the Φ scan an epitaxial relationship of $SrZrO_3$ $(0k0)$ [101] and MgO(001) [200] is deduced. This epitaxial relationship corresponds to the minimum mismatch of $f = 2.4\%$ (see Table I).

To investigate the influence of the deposition parameters on the film properties, growth temperature and oxygen pressure were varied. Furthermore, the influence of the *in situ* annealing step was examined. Decreasing the growth tem-

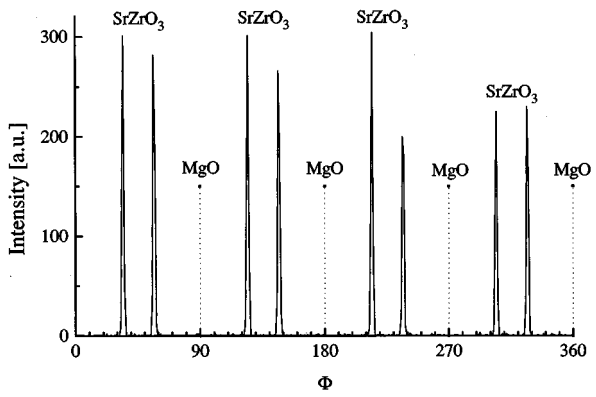

FIG. 3. Φ scan of the $SrZrO_3$(561) and $SrZrO_3$(165) reflections. Positions of the MgO(420) reflections are indicated by the dotted lines. The eight reflexes from the $SrZrO_3$ demonstrate the quasitetragonal structure of $SrZrO_3$.

perature causes a continuous increase of the minimum yield in RBS/C measurements. For growth temperatures lower than approx. 800 °C, no channeling was observed. Increasing the temperature up to 1200 °C, the maximum value of our heater, did not further improve the films. RBS/C minimum yield values stayed constant for heater temperatures of 1000–1200 °C. For these samples, the subsequent annealing step causes no further reduction in RBS/C minimum yield values, but the FWHM of the rocking curve narrows by approx. 0.1°. The second parameter to be varied is the oxygen background pressure during deposition. The further increase of this pressure is not useful because this leads to a smaller plume of material and therefore to inhomogeneities in the resulting films. A decrease in oxygen pressure results in better homogeneity, but the crystalline quality is degraded. For example, the RBS/C minimum yield values are increasing to approx. 50% for 1.1×10^{-2} mbar.

In conclusion, we have demonstrated perfect epitaxial growth of single phase Y-doped $SrZrO_3$ films by PLD on MgO(001) substrates. These films are presently optically evaluated. Due to their high degree of perfection, these $SrZrO_3$ films carry a significant potential for fuel cell applications. The versatility of PLD will easily permit future changes of stoichiometry or additional doping, if the demand arises.

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