SURFACE and INTERFACE ANALYSIS

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The use of low-energy SIMS (LE-SIMS) for nanoscale fuel cell material development

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Low-energy secondary ion mass spectrometry has been used to investigate the matrix structure and interface attributes of a novel $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ multilayer fuel cell material. Nanoscale oxide systems have shown enhanced ionic conductivities when produced to form highly oriented epitaxial structures. The Sm-doped CeO_2 material system is of particular interest for fuel cell technology because of its inherently high ionic conductivity at low operating temperatures (600–800 °C). For this study, a nanometer-scale $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ multilayer was grown by pulsed laser deposition. The sample was annealed at 700 °C in an oxygen ambience. High-resolution, low-energy depth profiling using Cs revealed some diffusion of the multilayer structure after annealing, along with a possible volume change for the Sm-doped layers. Changes in layer volume will lead to an increase in the mechanical strain and may cause the material to crack. The findings presented here suggest that the $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ multilayer structure in its current form may not possess the level of thermal stability required for use within a fuel cell environment. **Copyright © 2010 John Wiley & Sons, Ltd.**

Keywords: SIMS; fuel cells; nanoscale multilayers

Introduction

There is significant interest being shown in the use of ceria-based electrolytes as the material of choice for solid oxide fuel cells (SOFC), especially at the lower to intermediate temperature range (600–800 °C). These electrolytes possess higher ionic conductivities than the commonly used yttria-stabilized zirconia (YSZ),[1–3] and when doped with di- or trivalent cations, form oxygen vacancies that can lead to an increased oxygen ionic conductivity.[4]

Further enhancement of the materials' conductivity has been achieved through the manipulation of their microstructures, with a doubling in conductivity found for ceria-based electrolytes,[4,5] enhancements of over eight orders for nanometer-scale layers of $SrTiO_3$/YSZ,[6] and a 50-fold increase for a highly oriented, thin (20 nm) film YSZ multilayer material,[5] compared to conventional microcrystalline ceramics or single crystals. To fully exploit these enhancements for intermediate temperature solid oxide fuel cells (IT-SOFCs), a better understanding of the structural properties of the material is required. Structural information may be enough to elucidate the cause for these enhancements observed, especially as it has been suggested that the enhanced conductivities observed in these nanoscale multilayers occurs at the layer interfaces.[5] Another important aspect is the thermal stability of these layers, especially given their elevated operating temperatures, a parameter that affects the performance and lifetime of the fuel cell.

In this work, a $CeO_2/(Ce_{0.85}Sm_{0.15})O_2$ multilayer has been grown by pulsed laser deposition (PLD). Pieces of the as-deposited material were annealed under typical fuel cell operating conditions. The as-grown and annealed multilayer structures were then characterized using low-energy secondary ion mass spectrometry (LE-SIMS) to resolve interfacial features and any stoichiometric changes within the individual layers. From this study, the structures resilience to temperature cycling were also explored.

Experimental

PLD was used to deposit a high-quality thin-film multilayer sample of $Ce_{0.85}Sm_{0.15}O_2$ (30 nm)/CeO_2(20 nm) onto a (100) orientated MgO substrate. Deposition was carried out with a flux of ~2.4 Jcm^{-2} in 10 mTorr of ultrahigh purity O_2 and at a temperature of ~475 °C. Reflection high-energy electron diffraction (RHEED) measurements were taken before and during the deposition to monitor the epitaxial growth progress. The sample was finally capped with 100 nm of MgO which was deposited as a blocking layer for future oxygen ion exchange experiments. The final structure was also analyzed using X-ray diffraction (XRD) to check the crystalline growth integrity and that lattice matching to the substrate had been achieved. Pieces of the sample were annealed for 5 h at 700 °C under a ^{16}O atmosphere to study the thermal stability of the layers under typical fuel cell operating conditions.

SIMS depth profiling of the samples was carried out using an Atomika 4500 SIMS instrument. The primary ion beam used was 1 keV Cs^+ with a beam current of ~20 nA and an impact angle of 45° from normal. An analysis area of 300 × 300 µm was used. Negative secondary ions were collected and these

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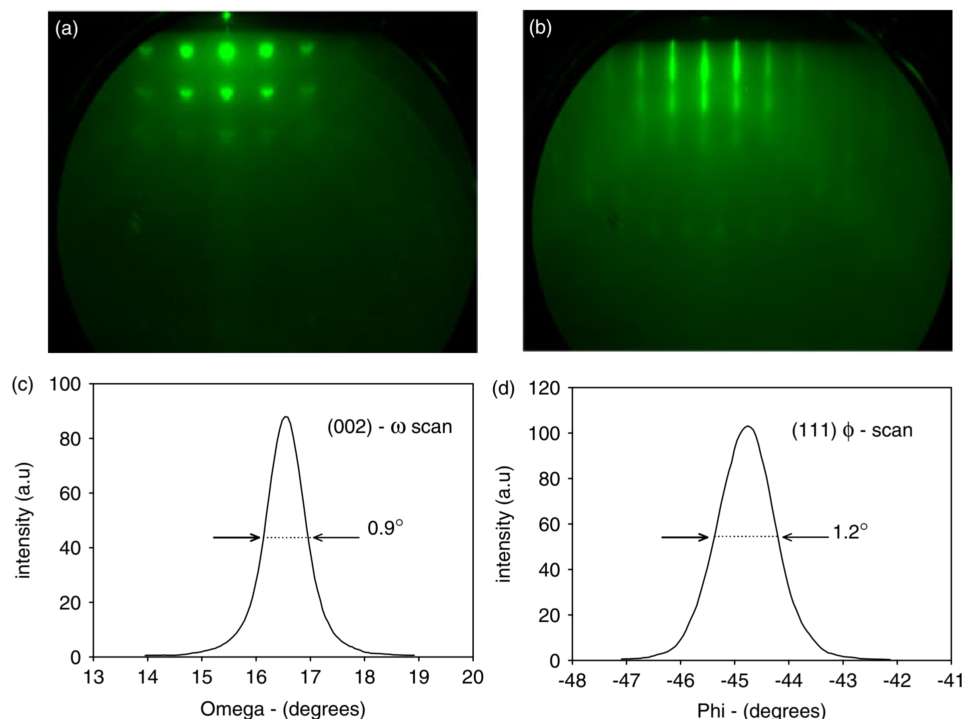

Figure 1. (a) A RHEED pattern from the MgO substrate prior to growth. (b) A RHEED pattern after deposition of the CeO_2 buffer layer. (c) Omega. (d) phi XRD scans of the multilayer structure after growth.

included both monatomic and polyatomic species: $^{16}O^-$, $^{140}Ce^-$, $^{156}CeO^-$ and $^{168}SmO^-$. Low-energy electrons were also used to charge compensate as the sample was insulating. The craters were measured using a stylus profilometer (Dektak 3030) for depth calibration. The erosion rate may vary between layers of different matrix composition,[7] and so, must be taken into consideration when calibrating the depth scale for a multilayer structure. To establish if this were the case here, depth profiles were taken from individual PLD-grown layers of CeO_2, $Ce_{0.85}Sm_{0.15}O_2$ and MgO under identical ion beam conditions. From these profiles some variation in the erosion rates were found: MgO (0.0356 nm/s), CeO_2 (0.0197 nm/s) and Sm-doped CeO_2 (0.0178 nm/s).

Results and Discussion

RHEED and XRD measurements were used to confirm that high-quality thin-film multilayers of $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ had been deposited onto a (100) MgO substrate. The spots observed in the RHEED pattern (Fig. 1(a)) taken from the MgO substrate before deposition indicated a rough starting surface. This rough substrate surface is believed to be a result of the phosphoric acid dip prior to deposition. The deposition of a CeO_2 buffer layer (approximately 50 nm thick) was found to significantly reduce the surface roughness as observed by streaks in the RHEED image, Fig. 1(b). These streaks were maintained throughout the entire growth process indicating smooth, crystalline epitaxial layers had been achieved. XRD measurements in the form of phi and omega scans from the final sample structure (Fig. 1(c) and (d)) reiterated that good cube-on-cube orientation had been achieved, and so confirming the material was of good crystalline quality and aligned to the underlying substrate.

The SIMS depth profiles taken from the as-deposited and annealed multilayer structures are shown in Fig. 2(a) and (b). A few different primary beam species (Ar, N_2 and Cs^+) were initially trialed, but the Ar and N_2 failed to produce a useable secondary ion yield enhancement compared with Cs^+. The erosion rates established from the single layers were used to accurately calibrate the depth scale.

The depth profiles show that the intended multilayer structure had been achieved with modulation of the Sm and Ce signals varying in accordance with the growth sequence. Also, the MgO capping layer which had been applied as a blocking layer for future ^{18}O exchange experiments was also determined to be of the intended (100 nm) thickness when its erosion rate was accounted for.

Figure 2(a) shows the SIMS profile for the as-deposited sample from which it is observed that sharp interfaces exist between the layers. Figure 2(b) shows the SIMS profile from the sample after annealing under a ^{16}O atmosphere for 5 h. Here, we see the annealing appears to have modified the structure when we compare Fig. 2(a) and (b). This can be seen more clearly when we normalize the data and plot it on a linear scale (Fig. 3(a) and (b)). For the as-deposited sample, Fig. 3(a), the $^{16}O^-$ and $^{156}CeO^-$ signals are seen to be sharp and symmetric. There is a slight loss of dynamic range with depth and this is most likely due to a small amount of beam-induced roughening. For the annealed sample, Fig. 3(b), the trailing edge of the $^{156}CeO^-$ signal shows the onset of diffusion, while the $^{16}O^-$ signal is also more diffuse throughout the structure.

The RHEED measurements, XRD scans and SIMS depth profiles for the as-deposited sample all indicate that a high-quality multilayer sample of $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ and of the intended layer thicknesses had been grown by PLD. From the SIMS profiles, no indication of growth segregation was found as sharp interfaces

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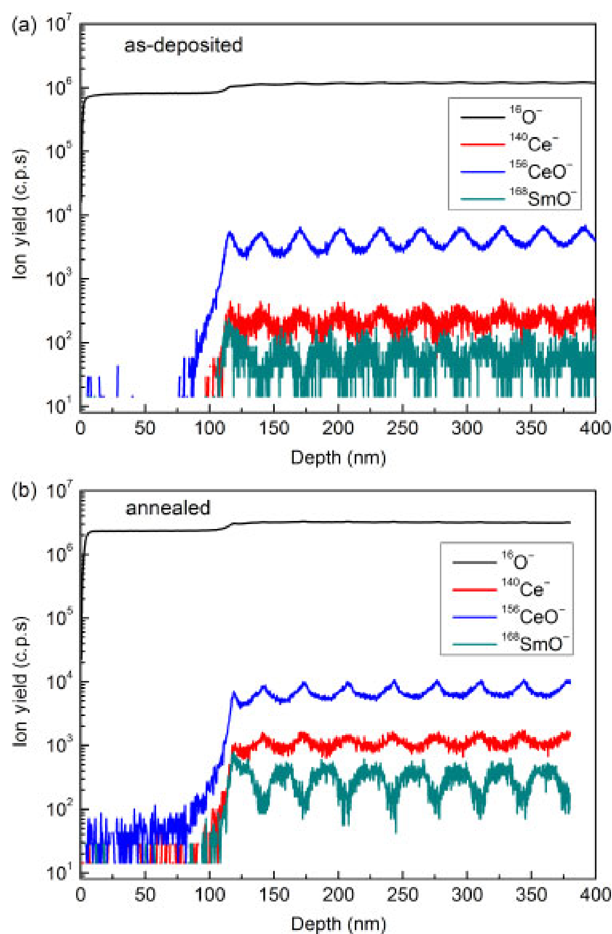

Figure 2. 1 keV Cs^+ SIMS depth profiles of the MgO-capped PLD-grown $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ multilayer sample: (a) as-deposited; and (b) 5-h-annealed sample.

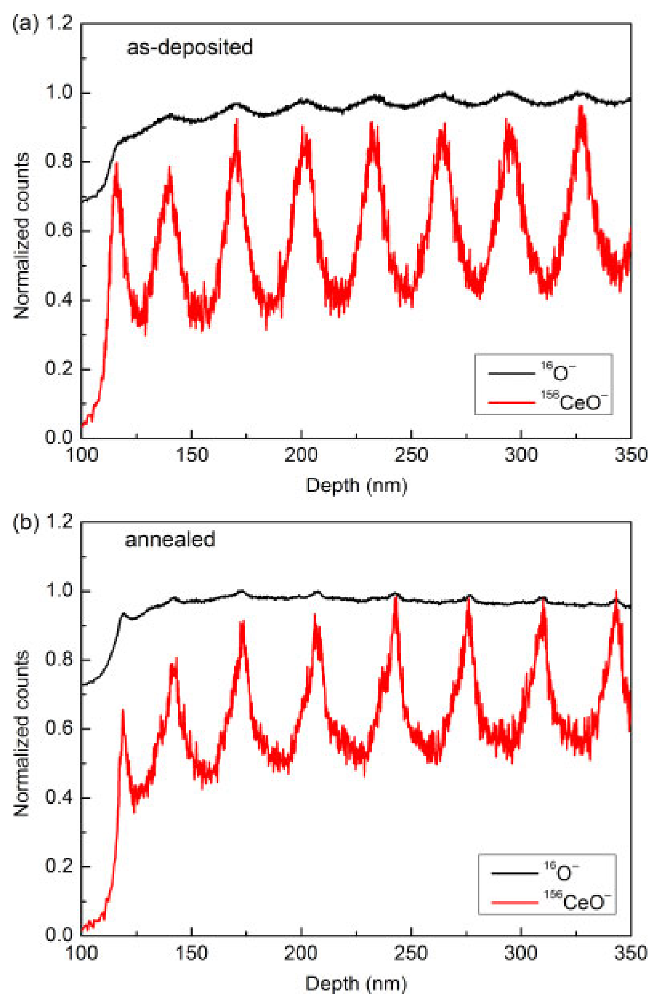

Figure 3. Comparison of the $^{16}O^-$ and $^{156}CeO^-$ signals obtained from the MgO-capped PLD grown $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ multilayer sample: (a) as-deposited; and (b) annealed.

between each layer were observed. After annealing, tails within the trailing edge of the $^{156}CeO^-$ and $^{16}O^-$ signals from the undoped layer were observed, a clear indication of diffusion. A deterioration of the interface quality would almost certainly be detrimental to the ionic conductivity. In particular, it would diminish any enhanced ionic conductivity that may exist along the interface region. Further work is therefore needed to identify how much diffusion occurs over successive thermal cycles, while some form of diffusion barrier may be required in future to prevent this diffusion but without affecting the interface ionic enhancements.

After annealing, there also appeared to be a change in volume in the Sm-doped layer as the $^{168}SmO^-$ signals are seen to be broader. This potential volume change may be a result of oxidizing; a strong possibility, given the annealing conditions applied, i.e. an oxygen ambient. Given the elevated operating temperatures and ambient conditions that fuel cells operate in, it is essential that the multilayer structure used is thermally stable. Volume changes during operation will introduce mechanical stress and strain, and potentially lead to cracking and the device to fail.

Conclusion

A nanometer-scale $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ heterostructure being developed for future fuel cells was grown using PLD. RHEED and XRD measurements confirmed that highly crystalline material had been deposited and was aligned to the (100) MgO substrate. LE-SIMS depth profiling revealed that sharp layer interfaces were achieved and that the layers deposited were of the intended dimensions.

After annealing under conditions representative of those typically used for fuel cell operation, some diffusion of the $^{16}O^-$ and $^{156}Ce^-$ was observed. This diffusion will affect the interface quality and diminish any enhanced ionic conductivity that may exist in this region. Annealing was also found to change the volume of the Sm-doped layers, with oxidization being suggested as the cause. Such changes in volume could lead to the fuel cell material cracking and the device to fail. The findings presented here suggest that the $Ce_{0.85}Sm_{0.15}O_2/CeO_2$ multilayer structure is not of sufficient thermal stability to operate within the fuel cell environment at this current time.

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