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Enhanced conductivity in pulsed laser deposited Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$/SrTiO$_3$ heterostructures

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Significant enhancement in the electrical conductivity of Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$ (CGO) thin films (250 and 500 nm) deposited on MgO(001) substrate is observed by introducing ~50 nm thick SrTiO$_3$ buffer layer film. Introduction of the buffer layer is found to form epitaxial films, leading to minimal grain boundary network that results in a free conduction path with near-zero blocking effects perpendicular to current flow. The in-plane conductivity measurements confirm increase in conductivity with increase in compressive strain on CGO films. © 2010 American Institute of Physics. doi:10.1063/1.3497294

Gadolinium doped ceria is a well-known oxygen ionic conductor for applications such as solid oxide fuel cells (SOFCs), gas sensors, and gas separation membranes.\textsuperscript{1,3} Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$ (CGO) exhibit larger ionic conductivity than yttrium stabilized zirconia, the conventional fuel cell electrolyte.\textsuperscript{4-5} There is a huge interest to obtain ionic thin films with less Ohmic resistance, scaling linearly with thickness, thus operating at lower temperature.\textsuperscript{6} CGO deposited on LSM and annealed at 1000 °C for 12 h prior to the impedance measurements for good contact formation. The impedance results from representative MgO electrode deposited onto the GCO film surface. LSM electrodes have high electronic conductivity and thermal expansion and ensure perfect adherence and full coverage of CGO at all temperatures. Au current collectors onto La$_{0.6}$Sr$_{0.4}$MnO$_{3-\delta}$ (LSM) electrodes deposited onto the GCO film surface. LSM electrodes have high electronic conductivity and thermal expansion and ensure perfect adherence and full coverage of CGO at all temperatures. Au current collectors were deposited on LSM and annealed at 1000 °C for 12 h prior to the measurements for good contact formation. The impedance spectra were correlated with dc measurements to monitor electrode contribution.

CGO target was prepared from commercial powder (Rhodia, Purity 99.99%) by 120 MPa uniaxial pressure followed by sintering at 1500 °C for 24 h. Pulsed laser deposition using KrF laser (248 nm) was used to deposit STO (50 nm) and CGO (250 and 500 nm) thin films on MgO(001) substrate. STO films were deposited at oxygen partial pressure $P_{O_2}$ of 0.1 mbar, maintaining substrate temperature at 760 °C, and frequency of 2 Hz. After the deposition the STO film was cooled to room temperature at 10 °C per min rate in 1 mbar $P_{O_2}$. Similarly, CGO films were deposited at $P_{O_2}$ of 10^{-2} mbar, substrate temperature of 750 °C, and frequency of 10 Hz with a cooling rate of 10 °C per min. Growth rate was 0.8 nm/min (2 Hz) and 4 nm/min (10 Hz) for the STO and CGO thin films respectively. The electrical properties were studied by both AC impedance and two-probe dc techniques in the temperature range 450–900 °C in air using gold (Au) current collectors onto La$_{0.6}$Sr$_{0.4}$MnO$_{3-\delta}$ (LSM) electrodes deposited onto the GCO film surface. LSM electrodes have high electronic conductivity and thermal expansion and ensure perfect adherence and full coverage of CGO at all temperatures.

Figures 1(a) and 1(b) show x-ray diffraction (XRD) patterns from representative MgO(001)/STO$_{50}$ nm and MgO(001)/STO$_{50}$ nm/CGO$_{250}$/500 nm films. These reveal the cubic fluorite structure of CGO films deposited on MgO(001)/STO$_{50}$ nm with no evidence of secondary phases. Only (h00) diffraction peak was detected indicating that the epitaxially grown STO$_{50}$ nm film with [100] direction perpendicular to substrate surface [Fig. 1(b)].

The lattice constant (a) of STO film is 3.924 Å, slightly larger than that in bulk STO (3.907 ± 0.001 Å), showing that the STO$_{50}$ nm film is in-plane compressed. The relative strain (s) is estimated from the relation, $s=(a-a_{\text{bulk}})/a_{\text{bulk}}$, where $a_{\text{bulk}}$ is the lattice constant of bulk. STO$_{50}$ nm film exhibited 0.45% strain leading to misfit of 2.3% between STO$_{50}$ nm buffer layer and CGO film. Similarly CGO$_{250}$ nm and

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CGO$_{250}$ nm films deposited on MgO/STO$_{50}$ nm resulted in 0.12% and 0.09% strain in CGO lattice. These small values of strain indicate higher structural coherence in CGO films deposited on STO$_{50}$ nm buffer layer. However, the FWHM of strain indicate higher structural coherence in CGO films.

The $\Phi$ scan on (301) peak of STO in MgO/(001)/STO$_{50}$ nm films show four distinct peaks with same intensity and nearly 90° spacing between peaks (Fig. 2). Similar trend was observed for CGO/(311) reflection, with a displacement of 45° with respect to MgO/(311). Epitaxial growth of CGO/(001) on MgO/(001) with STO$_{50}$ nm buffer layer has been achieved through rotation of CGO lattice by 45° with respect to STO lattice. This clearly indicates that epitaxial CGO films were realized on STO$_{50}$ nm basal plane (5.54 Å) due to low misfit compared to MgO/(001). The XRD patterns of MgO/STO$_{50}$ nm/CGO$_{250}$ nm heterostructures taken after electrical transport measurements at high temperature showed that the films retained their crystalline quality and, most important, the CGO is perfectly coherent with the STO, in agreement with XRD results, meaning that the CGO$_{250}$ nm layer grows rotated by 45° around the c axis and strains to match the STO basal plane. Increasing CGO thickness to 500 nm, it resulted in lowering of strain to 0.09%.

Figure 3(a) shows impedance spectra measured in air at 400 °C for MgO/(001)/CGO$_{250}$ nm, MgO/(001)/STO$_{50}$ nm/CGO$_{250}$ nm, and MgO/(001)/STO$_{50}$ nm/CGO$_{500}$ nm films. The spectra consist of a single non-depressed semicircles and no electrode feature is apparent in the spectra because their low impedance contribution. A single RC element (i.e., a resistor in parallel with a capacitor) is used as equivalent circuit to obtain the impedance-frequency relation at various temperatures. A single impedance arc of the polycrystalline CGO thin films is ascribed to total contribution of the grains and grain boundaries to the ionic conductivity. The total resistance of the sample is measured as the diameter of the semicircle. Frequency distribution shows the RC relaxation times for the samples at 400 °C measured as the diameter of the semicircle.
The conductivity curves shift upwards in films with \( \text{MgO} \) from Nyquist plots and \( \text{CGO}_{250} \) and \( \text{MgO} \) reported for bulk doped ceria.\(^{21}\) Larger conductivity than in the films deposited on \( \text{MgO} \) substrate. At 900 °C, total conductivity is found to be 3.7 \( \times 10^{-11} \) S/cm, 5.1 S/cm, and 12.1 S/cm for \( \text{MgO}(001)/\text{CGO}_{250} \) and \( \text{MgO}(001)/\text{STO}_{50} \) samples, respectively. The conductivity curves shift upwards in films with \( \text{STO}_{50} \) buffer layer. The calculated activation energies for \( \text{MgO}(001)/\text{STO}_{50} \) films were 0.93 and 0.94 eV. These activation energies correspond to the values reported for bulk doped ceria.\(^{21}\)

For coherent epitaxial growth, the lattice mismatch between thin film and substrate is accommodated entirely by strain within the film. As the film grows thicker the total strain energy in the film increases rapidly. The relaxation of this strain field determines the final film crystallinity. Mostly, the strain field caused by the lattice mismatch will be relaxed by generating dislocations and local lattice distortions, distribution of which strongly influence the film crystallinity. Large regions of lattice distortions may result in a columnar or polycrystalline growth, degrading the film quality and thus reducing the conductivity.\(^{9,22,23}\) In our \( \text{MgO}(001)/\text{STO}_{50}/\text{CGO}_{250}/500 \) heterostructures, the presence of uniformly strained regions lead to epitaxial nearly single crystal films. The increase in conductivity is attributed to negligible number of grain boundaries perpendicular to current flow. Conductivity enhancements open up exciting opportunities for oxide ionic conductors in technologies such as SOFCs.