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Room temperature epitaxial growth of (001) CeO_2 on (001) $LaAlO_3$ by pulsed laser deposition

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The room temperature epitaxial growth of CeO_2 on lattice matched (001) $LaAlO_3$ substrates by using pulsed laser deposition (PLD) method under various oxygen partial pressure (Po_2) is demonstrated. X-ray diffraction analysis with 2-Theta/rocking curve/Phi-scan, cross-sectional transmission electron microscopy with selected-area diffractions are used to characterize structural of grown films. The epitaxial (001) CeO_2 can be achieved at room temperature under Po_2 less than 2×10^{-3} Torr. The best quality of grown film is obtained under $Po_2 = 2 \times 10^{-5}$ Torr and degraded under $Po_2 = 2 \times 10^{-6}$ Torr due to oxygen deficiency in structure. The epitaxial relationship between CeO_2 and LAO is confirmed to be (001)CeO_2 //(001)LAO, $[100]_{CeO2}//[110]_{LAO}$ and $[010]_{CeO2}//[\bar{1}10]_{LAO}$. No obvious reduction reaction occurred, from Ce^{+4} turned into Ce^{+3} states, as reducing oxygen partial pressure during growth by PLD.

1 Introduction

CeO_2 is a remarkable functional oxide material with the nature of high dielectric constant (>25), lattice matching with Si [1], high melting point (2600°C), high chemical stability [2], good transmission in the visible regions [3], high efficiency for absorbing ultraviolet (UV) radiation [4]. Therefore, CeO_2 films have received intense interest in the field of gate insulator material for metal-oxide-semiconductor transistors [5], nonvolatile memory devices [6], silicon-on-insulator structures, capacitor devices [7,8] and solar cells [9]. Besides, CeO_2 is a promising electrolyte material of solid oxide fuel cells [10,11] and also proven to be an excellent buffer layer for high-temperature superconducting thin films [12].

To date, a great deal of efforts has focused on the epitaxial growth of CeO_2 [12–16]. Among the oriented surface of CeO_2, the (100) plane of the fluorite structure is unstable compared with the (110) or (111) planes due to a nonzero surface dipole [17,18] and would be a favorable surface with more reactive for catalytic films [19]. Various substrates have been used to achieve desired (100) orientation of CeO_2 epitaxial films, including metals, Si, and oxides such as r-cut Al_2O_3, MgO, $SrTiO_3$, $LaAlO_3$ and yttria-stabilized zirconia (YSZ) [13–16,20]. Among the single crystal substrates, $LaAlO_3$ (LAO) is a promising substrate for high quality Cerium oxide growth due to the slight lattice mismatch of about 0.95% ($a_{LAO} = 3.79$ Å, $a_{CeO} = 5.41$ Å) by simply rotating 45° in the CeO_2 basal plane conjunct on LAO. There are few of literatures reported the growth of CeO_2 on LAO, but the growth temperatures were all higher than 600°C [15,16]. It is well known that the better structural properties of grown films almost are obtained at higher substrate temperature. However, no literature regarding that the epitaxial growth of (001) CeO_2 can be achieved at room temperature.

In this work, we use pulsed laser deposition (PLD) method to study the epitaxial growth of CeO_2 on lattice matched LAO at room temperature. PLD is convinced to be an extraordinary technique for epitaxy at low temperature [21,22], because that the laser-ablated species impinging on the substrate inherent a large kinetic

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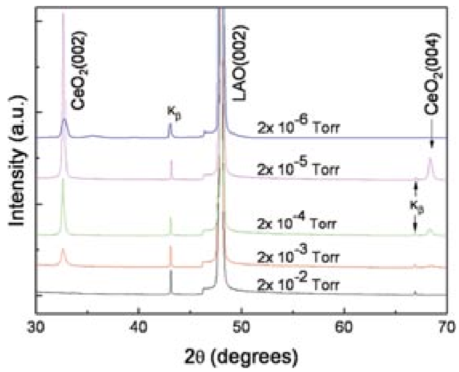

Fig. 1 X-ray 2-theta spectrum of CeO_2 films grown on LAO substrate under various oxygen partial pressures (Po_2).

energy which would enhance surface migration for epitaxy. A wide range of oxygen partial pressures (Po_2) is adopted to modulate the kinetic energy of Ce ion during growth. Based on this idea, the (100) CeO_2 epitaxy grown on LAO is achieved even at room temperature (RT). The effect on the Po_2 during growth and characterization of the grown CeO_2 films are presented.

2 Experimental

The growth of CeO_2 films were grown in DCA PLD500 PLD system. The ablation source we adopted is pulsed KrF-excimer laser of 248 nm wavelength with 25 nsec duration. A 2-inches circular CeO_2 target (99.99% purity) was used for ablation. After being cleaned in boiling acetone and isopryl alcohol, a $LaAlO_3$ (100) substrate in 2-inches diameter was loaded into the PLD chamber. The back ground pressure of growth chamber is evacuated down to 5×10^{-7} Torr. The oxygen partial pressure (Po_2) during deposition of CeO_2 was varied in the range of 2×10^{-2} to 2×10^{-6} Torr at room temperature. The laser energy density of 2–3 J/cm^2 with 3 Hz repetition frequency was used for growth. To monitor the surface morphology during growth, RHEED patterns were taken from an Oxford Scientific OS-RHEED system operated at 15 kV. The crystallinity of CeO_2 thin films was examined using a Bruker D8 x-ray diffractometer for 2-Theta scan and for Phi-scan. Transmission electron microscopy (TEM) for microstructural observations in cross section was performed in a FEI Tacnai 20 microscope. In addition, chemical surface analyses of the grown films were performed by using an x-ray photoelectron spectrometer (XPS).

3 Results and discussion

Figure 1 shows the XRD θ-2θ spectrums of CeO_2 films grown on (001) LAO at room temperature under various oxygen partial pressures (Po_2). In figure 1, there is no obvious peak from the diffraction of CeO_2 (002) as deposited under $Po_2 = 2 \times 10^{-2}$ Torr. The weak intensity of diffractions form (002) CeO_2 reveals that amorphous phase is formed in the film. As decrease the Po_2 during deposition, the diffraction intensity of peaks from (002) CeO_2 getting larger from the range of 2×10^{-3} to 2×10^{-5} Torr. The maximum peak intensity of (002) CeO_2 is obtained under $Po_2 = 2 \times 10^{-5}$ Torr condition, suggesting that the cubic on cubic growth of (001) oriented CeO_2 on (001) LAO are strongly dependent on Po_2 during pulsed laser deposition.

PLD is considered as a method with great potential of epitaxial growth at RT due to its high kinetic specs of plume. L. G. Coccia et al. have indicated in their studies that the count distribution of Ce+ ions with energy of 20 eV is strongly related to the background pressure during ablation from CeO_2 [23]. When the sample grown by PLD under high background of 2×10^{-2} Torr, the high kinetic species generated from excimer laser ablation will collide with background gas molecular inducing high bright plume and loss energy [24]. Accordingly, an amorphous phase of CeO_2 is formed in this condition. On the contrary, as PLD grown under low background pressure, the Ce+ ions would preserve more kinetic energy during growth and move to the stable's site. That is the reason why the less Po_2 during growth the higher intensity of (002) CeO_2 diffractions is observed. The best quality of epitaxy CeO_2 on LAO is obtained under $Po_2 = 2 \times 10^{-5}$ Torr condition at room temperature.

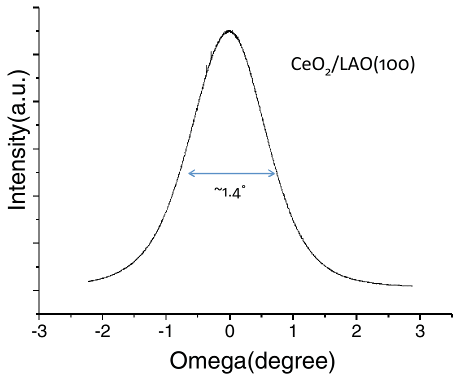

Fig. 2 X-ray rocking curve spectrum of CeO_2 grown on LAO substrates under $Po_2 = 2 \times 10^{-5}$ Torr.

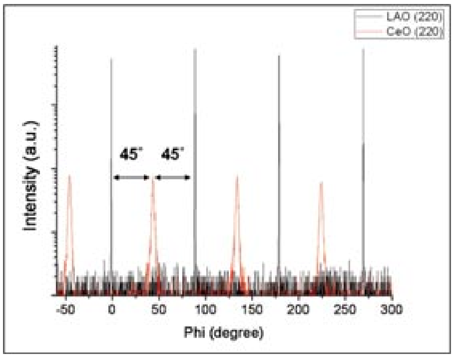

Fig. 3 X-ray phi-scan spectrum of CeO_2 film and LAO substrate. The growth of CeO_2 conjunct on LAO with 45° rotation is confirmed.

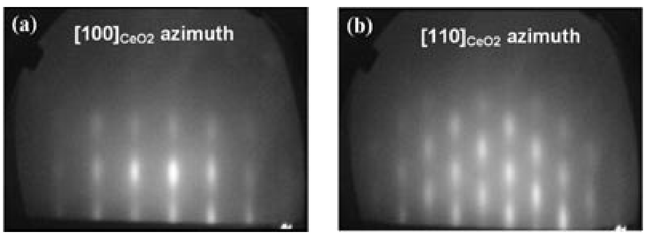

Fig. 4 The RHEED pattern of CeO_2 grown on LAO under $P_{O2} = 2 \times 10^{-5}$ Torr at room temperature. (a) The image taken along $[100]_{CeO2}$ azimuth. (b) The image taken along $[110]_{CeO2}$ azimuth.

According to the XRD analysis, the best crystalline quality of (002) CeO_2 grown under 2×10^{-5} Torr is obtained with FWHM in X-ray rocking curve of 1.4° (as shown in figure 2). However, as the Po_2 decrease to 2×10^{-6} Torr, the intensity of (002) CeO_2 diffractions is going down inversely. It might because of the oxygen deficiency induced degradation of crystalline during growth under the extremely low background pressure.

To realize the epitaxial relationship of CeO_2 grown on LAO at RT, X-ray phi-scan analysis was performed on the best quality sample grown under $Po_2 = 2 \times 10^{-5}$ Torr condition. As shown in figure 3, the LAO (220) and CeO_2 (220) reflection peaks with 45° offset are observed within 0~360 phi-degree. It suggests that the epitaxy of CeO_2 grown on substrate (LAO) conjuncts with 45° rotation. A lattice mismatch of 0.94% between CeO_2 and LAO can be estimated by $(a_{CeO2} - \sqrt{2}a_{LAO})/\sqrt{2}a_{LAO}$. Therefore, the epitaxial relationship between CeO_2 and LAO should be controlled by the minimum lattice mismatch and determined as: $(001)_{CeO2}//(001)_{LAO}$ and $[100]_{CeO2}//[110]_{LAO}$.

To monitor the surface of grown films, a reflective high energy electron diffraction (RHEED) was used. Figure 4(a) and 4(b) show the RHEED patterns along [100] and [110] azimuth of CeO_2 grown on LAO (001) under $P_{O2} = 2 \times 10^{-5}$ Torr, respectively. Comparing the RHEED patterns with diffractions pattern of cubic

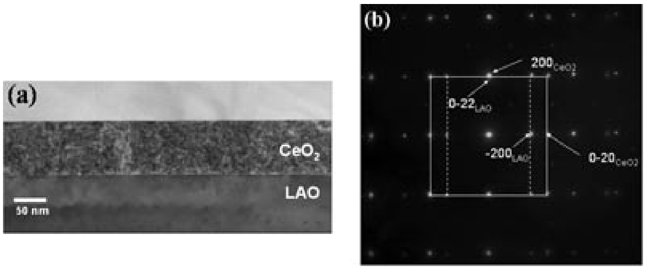

Fig. 5 (a) The cross-sectional TEM image along $[110]_{LAO}$ azimuth, (b) selected area diffractions of (a) of CeO_2 grown on LAO substrate at RT under $P_{O2} = 2 \times 10^{-5}$ Torr.

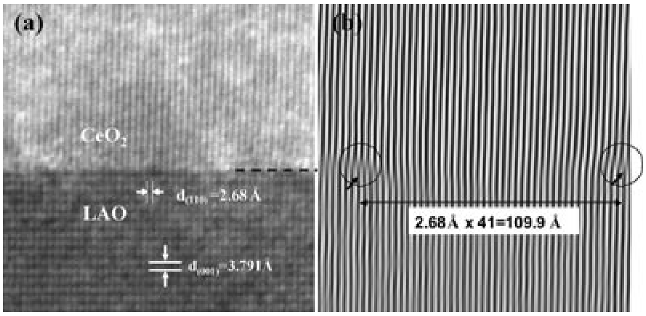

Fig. 6 (a) HRTEM image of CeO_2 grown on LAO under $P_{O2} = 2 \times 10^{-5}$ Torr at room temperature along $[100]_{CeO2}$ and $[110]_{LAO}$ azimuth. (b) The Inverse Fast Fourier Transform image of (a). The period of misfit is indicated as 109.9Å.

model, single crystal CeO_2 with cubic structural epitaxy can be confirmed. Besides, the spotty patterns of figure 4(a) and 4(b) reveal a 3-D growth mode occurred. It might due to the high supersaturation growth condition at room temperature.

In order to study the microstructure and crystallinity, a cross-sectional transmission electron microscopy (TEM) was proceeded on the sample of CeO_2 grown under $PO_2 = 2 \times 10^{-5}$ Torr as shown in figure 5. Figure 5(a) is the bright field cross-sectional TEM image along $[110]_{LAO}$ azimuth. An about 100 nm thickness of CeO_2 with sharp interface between substrate was clearly observed. Figure 5(b) is the selected area diffraction pattern of CeO_2/LAO along $[110]_{LAO}$ azimuth. In figure 5(b), $[100]_{CeO2}$ diffraction pattern indexed with a solid line is clearly confirmed, implied that the purely epitaxial growth of single crystal CeO_2 grown on LAO at RT is achieved. The growth relationship can be determined as: $(001)_{CeO2}//(001)_{LAO}$, $[100]_{CeO2}//[110]_{LAO}$ and $[010]_{CeO2}$ // $[\bar{1}10]_{LAO}$ and consistent with the result of X-ray ϕ-scan examination as shown in figure 3.

Figure 6(a) is the high resolution cross-sectional TEM image of CeO_2 on LAO along $[100]_{CeO2}$ and $[110]_{LAO}$ azimuth. A clear lattice image at the interface without interlayer is observed, suggesting good crystallinity of single crystal CeO_2 can be achieved by PLD even at RT. To examine the period of misfit dislocations which is strongly correlated to the lattice mismatch of grown film and substrate, the Inversed Fast Fourier Transform (IFFT) of selected HRTEM image were performed. Figure 6(b) is the Inverse Fast Fourier Transform (IFFT) image of figure 6(a). The misfit dislocation sites are indicated in figure 6(b) to estimate the distance between the two misfits as 109.9 Å. From the small lattice mismatch of about 1% between CeO_2 and LAO, as well as the in plane translation period of $d_{LAO(110)}$ is 2.68 Å, a misfit dislocation period of ∼268 Å can be calculated by theory (∼2.68 Å/0.01). The distance between two misfits is over 2 times less of the period we estimated, suggesting that there is still higher density of misfit dislocations existed in the single crystalline CeO_2 grown at room temperature by PLD.

Figure 7 shows core level x-ray photoelectron spectra of Ce 3d peaks of CeO_2 grown under PO_2 from 2×10^{-3} to 2×10^{-5} Torr. The Ce 3d spectra exhibit complicated features due to shake-up and shake-down processes which have been extensively investigated [25–27]. The six peaks labelled of Ce^{+4} are corresponding to the Ce $3d_{3/2}$ and $3d_{5/2}$ spin–orbit components, respectively [26]. While the Ce^{+3} states labelled at the peak of ∼903 eV and 885 eV are according to Heikkinen et al. [27]. Comparing the Ce 3d spectra in figure 5, we can clearly observe that the sample grown under $Po_2 = 2 \times 10^{-5}$ Torr exhibit the strongest Ce^{+4} signal. That might

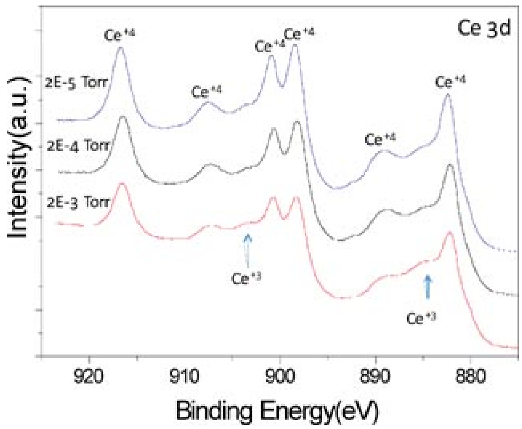

Fig. 7 XPS spectrum of Ce3d on CeO_2 grown films in various oxygen partial pressures during growth at room temperature by PLD. The binding energy of Ce^{+4} and Ce^{+3} states are indicated.

due to the best crystalline quality among these samples. However, there is not much difference in Ce^{+3} spectra as Po_2 decreasing. It suggests that no obvious reduction reaction occurred, from Ce^{+4} turned into Ce^{+3} states, while grown under reducing oxygen partial pressure by PLD.

4 Conclusion

An epitaxial (001) plane of CeO_2 film grown on lattice matched LAO substrate is achieved by PLD at room temperature. From the results of X-ray diffraction analysis, the oxygen partial pressure is a dominate factor in the epitaxial growth of (001) CeO_2. The (001) CeO_2 has the best quality grown under $Po_2 = 2 \times 10^{-5}$ Torr, but degrades at $Po_2 = 2 \times 10^{-6}$ Torr due to oxygen deficiency in structure. The epitaxial relationship between CeO_2 and LAO can be determined by X-ray phi-scan and TEM SAD as:$(001)_{CeO2}$//$(001)_{LAO}$, $[100]_{CeO2}$//$[110]_{LAO}$ and $[010]_{CeO2}$ // $[\bar{1}10]_{LAO}$. XPS analysis reveal that no obvious reduction reaction from Ce^{+4} turned into Ce^{+3} states is observed while grown under reducing oxygen partial pressure by PLD.

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