Effects of deposition conditions on the structural features of CeO_2 films prepared by laser chemical vapor deposition

From January to March 2011, I visited IMR of Tohoku University to work on the laser chemical vapor deposition of CeO_2-based films in collaboration with Prof. T. Goto. We studied the influence of deposition conditions on microstructure, orientation and deposition rates of CeO_2-based films.

The most notable property of CeO_2 is its capacity to release and store considerable amounts of oxygen while preserving its fluorite structure, a property known as the oxygen storage capacity (OSC) [1]. CeO_2 is known to experience Ce^{4+} to Ce^{3+} reductive and Ce^{3+} to Ce^{4+} re-oxidizing behaviors via charge compensating oxygen vacancy mechanisms. This property makes CeO_2 a technologically useful oxide. The growth of CeO_2 films is one alternative for enhancing the OSC. Favorable oriented films are of significant importance not only in semiconductor industry [2-3] but also in catalysis [4-6]. As a buffer layer, (100)-oriented CeO_2 films are attractive to achieve the preferred (100) epitaxial growth of semiconducting films. (100)-oriented films are also catalytically desirable since the CeO_2 (100) plane is unstable compared with (111) and (110) planes and consequently more reactive. In addition, the formation of oxygen vacancies on CeO_2 (100) plane requires less energy than on (111) plane, which is directly related to the OSC [7]. A highly porous morphology and the natural defective film structure may further enhance the catalytic performance of CeO_2 by facilitating the oxygen mobility and increasing the accessible catalytic sites.

CeO_2-based films were prepared on silica glass substrates (10 mm × 15 mm × 1 mm) in a hemispherical cold-wall type LCVD apparatus. A semiconductor InGaAlAs (808 nm in wavelength) laser beam was defocused to about 20 mm in diameter to irradiate the whole substrate. Ce-dipivaloylmethanate [$Ce(dpm)_4$] was employed as precursor. It was evaporated at 493 - 533 K and their vapors were carried by argon gas (flow rate: 50 - 200 cm^3/min) through a vertical nozzle separated 25 mm from the substrate. Oxygen gas was added (flow rate: 50-200 cm^3/min) through a concentric-vertical nozzle and mixed with the precursor vapors just above the surface substrate. Before deposition, the substrates were pre-heated (T_{pre}) from 473 to 873 K. While the laser power (P_L) was controlled from 0 to 200 W, the total pressure (P_{tot}) was varied from 0.4 to 0.8 kPa. Depositions were performed for 600 s. Deposition rates were estimated from cross-sectional film images. The crystal structure of the films was analyzed by typical θ-2θ X-ray diffraction measurements (XRD; Rigaku RAD-2C). The surface morphology and cross-sectional microstructures were investigated by field emission scanning electron microscopy (FESEM; JEOL JSM-7500F) and transmission electron microscopy (TEM; JEOL 2000 EXII, 200 kV).

Figure 1 summarizes the effects of T_{pre} and P_L on the structural features of CeO_2 films over the entire ranges investigated. P_{tot} was kept at 0.8 kPa. Without the influence of laser irradiation, i.e. P_L = 0, non-oriented films were obtained above T_{pre} = 573 K. In contrast, (100)-oriented films were often produced under the influence of laser irradiation even without the need of pre-heating (R.T.), when P_L = 150 - 200 W. Feather-like columnar grains were typically observed at oriented films, while those prepared at P_L = 200 W and especially at T_{pre} = 873 K exhibited dense and wider columns.

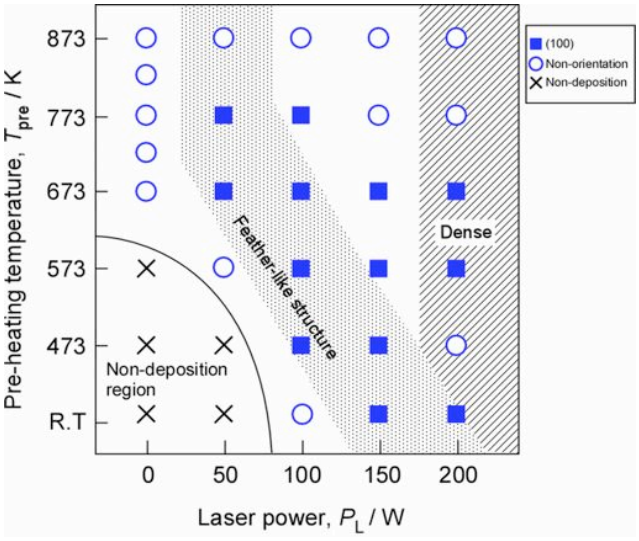

Figure 1. Effects of T_{pre} and P_L on the structural features of CeO_2 films.

Figure 2 presents the FESEM images of the cross-sectional structure and surface morphology of CeO_2 films prepared at T_{pre} = 673K, P_L = 50 - 150 W and P_{tot} = 0.8 kPa. A clear columnar structure was developed under laser irradiation, where the columns exhibited either pyramidal or flat top-endings mainly depending on P_L

conditions. Pyramidal ending columns were predominantly exposed. At P_L = 0, grains with no specific orientation and rather granular surface morphology were typically observed. Since the precursor vapors and the surface mobility of chemical species could be highly activated by laser irradiation, enhanced selective adsorption of oxygen on more reactive (100) surface may be accounted for a faster growth along [100] direction from initially randomly oriented grains.

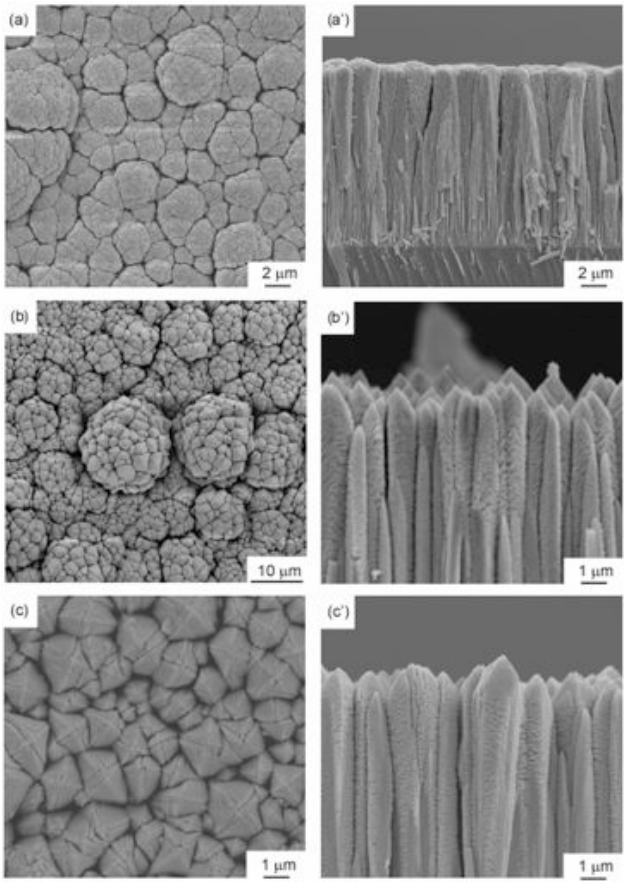

Figure 2. FESEM images of the cross-sectional structure and surface morphology of CeO_2 films prepared at T_{pre} = 673K, (a) P_L = 150, (b) P_L =100 and (c) P_L = 50 W.

Figure 3 shows the change of Lotgering factor (100) for CeO_2 films as a function of P_L and T_{pre}. Lotgering factor achieved values above 0.8 for most conditions producing oriented films. This implies a high degree of (100) orientation and the ability of LCVD to growth desirable oriented CeO_2 films. At P_{tot} = 0.4 - 0.6 kPa, however, films showed not only (100) but also (110) and (311) orientations. In summary, (100) preferred orientation was obtained at high total pressure (P_{tot} = 0.8 kPa) over the entire range of temperature (T_{pre} = 473 - 873 K), while (110) and (311) orientations were produced at low total pressure (P_{tot} = 0.4 - 0.6 kPa) .

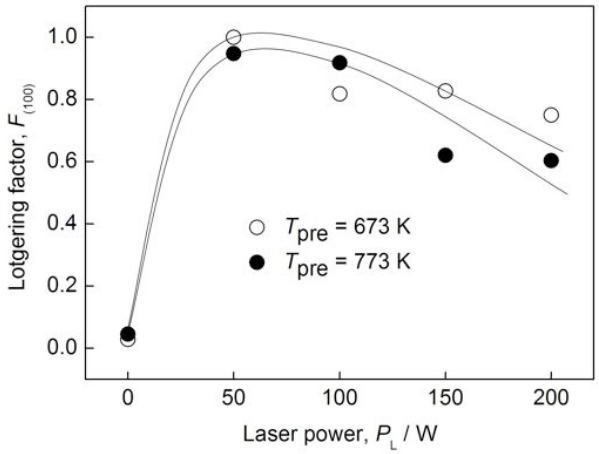

Figure 3. Change of Lotgering factor (100) for CeO_2 films as a function of P_L and T_{pre}.

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Key Words

Laser chemical vapor deposition, CeO_2 films, Oriented films

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