



Rh-nanoparticle-dispersed ZrO₂ films prepared by laser chemical vapor deposition

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ABSTRACT

Rhodium-nanoparticle-dispersed zirconia (Rh/ZrO₂) films were prepared by laser chemical vapor deposition using Rh and Zr dipivaloyl methane precursors. The effects of deposition conditions and heat treatment on the microstructures of ZrO₂ and Rh/ZrO₂ films were investigated. At a deposition temperature of 1180 K and a Rh to Zr source molar ratio ($R_{\text{Rh/Zr}}$) of 0.05, Rh nanoparticles precipitated on the surface of a (020)-oriented ZrO₂ matrix having a feather-like structure. The diameter of the Rh nanoparticles increased from 25 to 70 nm as $R_{\text{Rh/Zr}}$ increased from 0.01 to 0.10. The microstructure of the Rh nanoparticles and the feather-like structure of the ZrO₂ matrix were unchanged after heat treatment at 873 K in air for 10 h.

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1. Introduction

Noble metals, mainly the platinum group metals, have been used as catalysts in exhaust gas filters for automobiles and fuel cells [1,2]. In these applications, the consumption of noble metals should be minimal. Because catalytic reactions occur at the three-phase boundary of a gas, a catalyst and a support material, nanoparticles of noble metals can be dispersed on the support [3,4]. Furthermore, the surface area of the support should be maximized to reduce the amount of noble metals dispersed. Although Pt is the most common catalyst among the platinum group metals, its catalytic activity degrades in a CO–CO₂ atmosphere (CO poisoning). [2]. Thus, rhodium (Rh) can be a candidate catalyst because of lesser CO poisoning [5].

The support material should be porous with a large surface area and should have thermal stability under high-temperature operation over 700 K. Zirconia (ZrO₂) has a high melting point (2973 K) with high corrosion resistance and high strength, and thus is a promising support material [6]. Porous structures have often been prepared by the sol–gel method. However, a disadvantage of this method is that sol–gel films suffer from microcracking and agglomeration when dried at high temperatures. In contrast, dry processes, *i.e.*, physical vapor deposition (PVD) and chemical vapor deposition (CVD), can be used to prepare porous films by controlling deposition conditions [7–9]. Porous feather-like microstructures have been commonly observed in films prepared by electron beam PVD (EB-PVD) [10], and thus, EB-PVD has been also employed for preparation of various electrode films for fuel cells and sensors. However, EB-PVD may be unsuitable for preparing nanocomposite films because of difficulties associated with source materials and very low deposition efficiencies. Furthermore,

porous or feather-like structures cannot be prepared by sputtering, pulsed laser ablation and other PVD techniques.

CVD is a versatile technique for preparing nanoparticles and porous films [11], and various types of noble metal nanoparticles and films have been prepared by CVD using metal-organic precursors (MOCVD) [12]. We have employed laser CVD to prepare yttria-stabilized ZrO₂ [13,14] and alumina (Al₂O₃) [15,16] films having columnar grains with a porous feather-like structure. By combining these techniques, we can precipitate noble metal nanoparticles in porous films having a feather-like structure. In the current study, Rh-nanoparticle-dispersed ZrO₂ (hereafter Rh/ZrO₂) films were prepared by laser CVD. The effects of deposition conditions on the microstructure and thermal stability of Rh/ZrO₂ films were investigated.

2. Experimental procedure

Fig. 1 shows a schematic of the laser CVD apparatus. Rh(dpm)₃ and Zr(dpm)₄ (dpm: dipivaloyl methane) were used as precursors. Rh(dpm)₃ was heated between 456 and 518 K, and Zr(dpm)₄ at 523 K. The Rh/Zr source molar ratio ($R_{\text{Rh/Zr}}$) was controlled between 0.01 and 0.10. Precursor vapors and O₂ gas were separately introduced into the CVD chamber through a double-tube nozzle. The gas flow rates of the Ar carrier gases for Rh and Zr vapors and O₂ gas were fixed at $5.0 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$. The total pressure in the CVD chamber was kept at 0.93 kPa. An Al₂O₃ plate substrate (12 mm × 12 mm × 2.5 mm) was pre-heated on a hot stage at 273–973 K (T_{pre}). A Nd:YAG laser beam (continuous wave mode; wavelength: 1064 nm; Lee Laser, Series 800) was expanded by lenses and introduced in the CVD chamber through a quartz window to irradiate the entire substrate surface (approximately 20 mm in diameter). The laser power (P_L) was controlled between 0 and 206 W. The deposition temperature (T_{dep}) was measured with a thermocouple inserted into a groove of the substrate. Depositions

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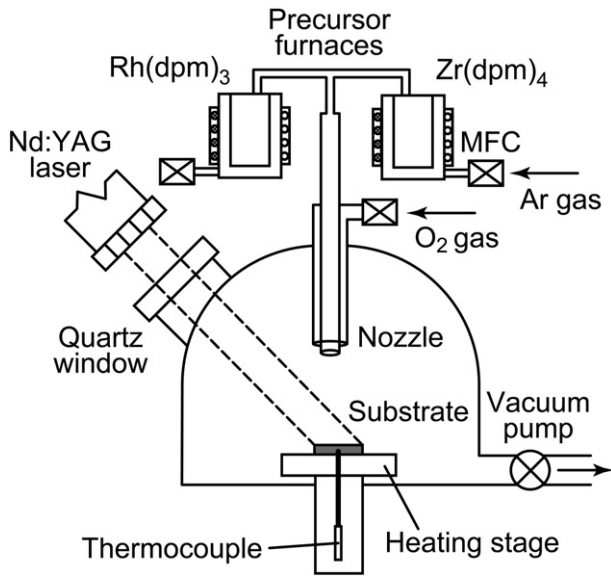


Fig. 1. Schematic of the laser CVD apparatus.

were conducted for 600 s. The Rh/ZrO₂ films were heat treated at 673–1473 K for 10 h in air.

The crystal structure was studied by X-ray diffraction (θ -2 θ XRD; Rigaku RAD-2C). The surface and cross-sectional microstructures were observed by a scanning electron microscope (SEM; Hitachi S-3100H), and the composition was measured using an energy dispersive X-ray spectroscope attached to a field emission scanning electron microscope (EDX-FESEM; JEOL JSM-6500FT). EDX spot size was 10 nm in diameter. Diameter of Rh nanoparticle was determined from the average of 30 nanoparticles counted in FESEM image. The deposition rate was calculated from the thickness and the deposition time.

3. Results and discussion

3.1. Preparation of ZrO₂ films

Fig. 2 shows the typical XRD patterns of the ZrO₂ films. At $P_L = 100$ W and $T_{pre} = 973$ K ($T_{dep} = 1074$ K), a mixture of monoclinic ZrO₂ (m-ZrO₂; space group: $P2_1/c$; $a = 0.5148$ nm, $b = 0.5206$ nm, $c = 0.5321$ nm; JCPDF #83-0942) and tetragonal ZrO₂ (t-ZrO₂; $P4_2/nmc$;

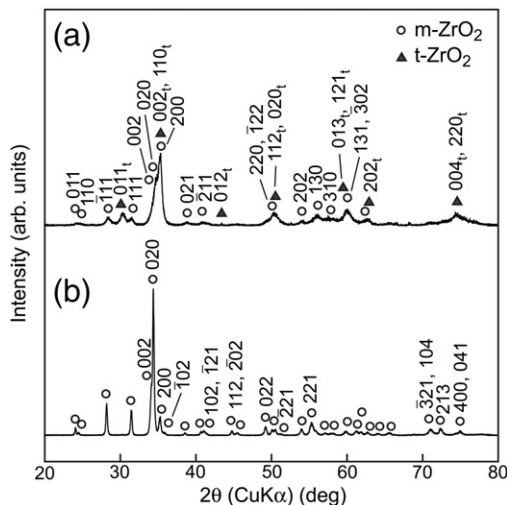


Fig. 2. XRD patterns of ZrO₂ films prepared at deposition temperatures of 1074 K (a) and 1183 K (b).

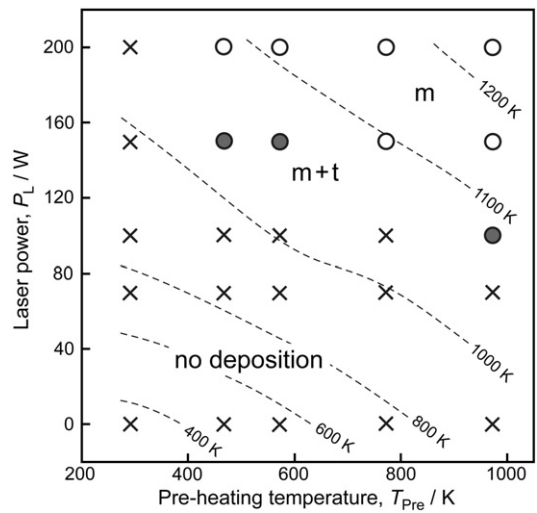


Fig. 3. Phase diagram as a function of preheating temperature and laser power. Open and filled circles indicate the formation of monoclinic ZrO₂ (m) and mixture phase of monoclinic and tetragonal ZrO₂ (m + t), respectively. The dotted line denotes the isothermal line of deposition temperature (T_{dep}).

$a = 0.3592$ nm and $c = 0.5179$ nm; JCPDF #79-1771) was obtained (Fig. 2(a)). Single phase (020)-oriented m-ZrO₂ films were prepared at $P_L = 200$ W and $T_{pre} = 973$ K ($T_{dep} = 1183$ K) (Fig. 2(b)). The lattice parameters of the films were calculated to be $a = 0.5086$ nm, $b = 0.5213$ nm and $c = 0.5249$ nm. Fig. 3 depicts the effects of P_L and T_{pre} on T_{dep} and the crystal structure of ZrO₂ films. The deposition temperature (T_{dep}) was controlled by P_L and T_{pre} , and the contour line of T_{dep} is depicted with dashed lines in Fig. 3. A mixture

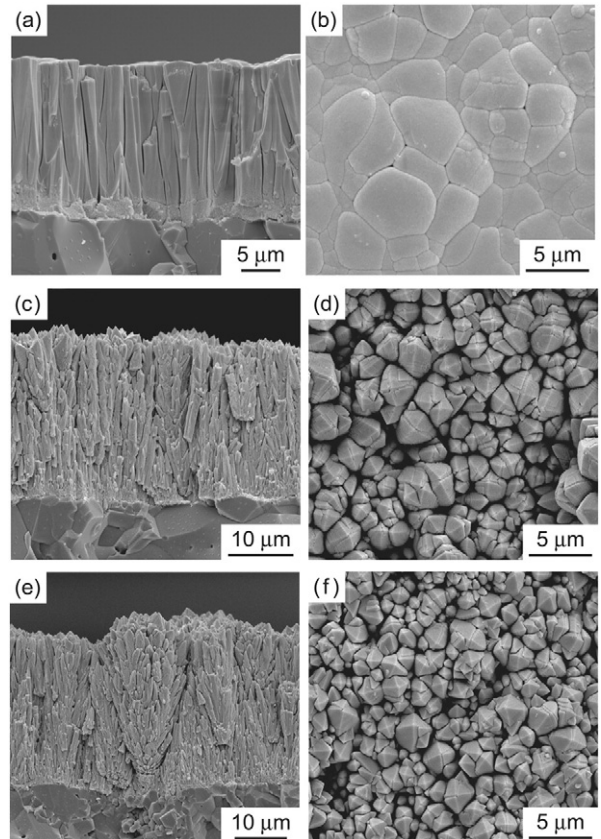


Fig. 4. Cross-sectional SEM images of ZrO₂ films prepared at various deposition temperatures: 1074 K (a, b), 1183 K (c, d), and 1228 K (e, f).

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