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High-speed oxide coating by laser chemical vapor deposition and their nano-structure

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Abstract

Oxide thick films, partially yttria-stabilized zirconia (YSZ) and titania (TiO_2), were prepared by laser chemical vapor deposition (LCVD). The assistance of laser tremendously increased the deposition rate for YSZ and TiO_2 films up to 660 and 2500 μm/h, respectively. The increase in the deposition rate was accompanied by plasma formation around the deposition zone, and the plasma was observed over critical values of laser power and substrate pre-heating temperature. A wide variety of morphologies of films from feather-like columnar to dense microstructures were obtained depending on deposition conditions. The columnar structure contained a large amount of nano-pores at columnar boundary and inside grains. These columnar structure and nano-pores were advantageous for applying YSZ films to thermal barrier coatings.

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1. Introduction

Laser-assisted chemical vapor deposition (LCVD) has been utilized to fabricate mainly thin films in semiconductor devise applications [1]. In general, LCVD can be categorized into two types; one is photolytic LCVD where laser is used as a high-energy source for photochemical reactions and the other is pyrolytic LCVD where laser is used as a heat-source for thermal reactions. Photolytic LCVD would often adopt ultra-violet laser with energy of several eV. The chemical reactions for the film deposition would proceed by high energy photon energy even without substrate heating. In pyrolytic LCVD, on the other hand, significantly high deposition rates have been achieved by focusing laser beam. However, the volume deposition rate (deposition rate in thickness multiplied by area) has been very small ranging around 10^{-12} to 10^{-8} m^3h^{-1}, where thin films, small dots and thin wires have been prepared [2]. A CO_2 laser with high power about several 100 W was employed in LCVD to prepare relatively thick materials such as TiN and TiB_2 several 10 μm in thickness [2]. However, pyrolytic LCVD using the CO_2 laser has not been widely utilized due to several difficulties such as absorption by window material; ZnSe could be commonly chosen to avoid absorption of an infra-red light.

On the other hand, the recent development of laser technology can provide usage of high-power laser with easiness. We have found that many oxide thick films can be prepared at high deposition rates more than several 100 μm/h by using LCVD [3,4]. This paper focuses on the preparation of yttria-stabilized zirconia (YSZ) and titania (TiO_2) films by LCVD using high power Nd:YAG laser.

Since YSZ films are chemically stable at high temperatures having a low thermal conductivity and good compatibility with Ni-base superalloy, they have been intensively investigated as thermal barrier coatings (TBCs) [5]. The thickness of TBCs should be more than several 100 μm, and therefore high-speed deposition processes commonly plasma spray [6] and electron-beam physical vapor deposition (EB-PVD) [7] have been employed. However, heterogeneous microstructures of thermal spray TBCs have often caused delaminating in a relatively short period. EB-PVD process is able to fabricate an appropriate columnar microstructure including nano-pores, which reduce the thermal conductivity; however, the nano-

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pores would easily disappear after heat-treatment. To develop long-life TBCs with low thermal conductivity, another route for high-speed deposition with superior controllability of microstructures should be pursued, because thermal conductivity, adherence to the substrate and thermal shock resistivity are strongly affected by the microstructures of the coating. We have reported high-speed deposition of YSZ films at 108 μm/h by using conventional thermal MOCVD [8]. However, the CVD process with much higher deposition rates would be required for practical applications.

TiO_2 films, on the other hand, have several advantageous characteristics such as photocatalysis, solar power generation and self-cleaning. TiO_2 has polytypes of anatase, rutile and brookite. Since anatase has better photocatalytic performance due to the wider energy band gap [9,10], anatase films in a single phase with high quality and large surface area have been preferably prepared. However, anatase would be a low-temperature form and the deposition rate decreases with decreasing temperature. Therefore, the conventional thermal MOCVD may be inappropriate to prepare thick anatase films.

This paper reports the high-speed deposition of YSZ and TiO_2 films by LCVD, and describes the effect of deposition conditions mainly on deposition rates, morphology and nanostructure.

2. Experimental

Fig. 1 demonstrates a schematic diagram of LCVD apparatus that was made of stainless steel with a hemispherical cold-wall type chamber. The laser light (Nd:YAG, continuous mode, $\lambda = 1064$ nm) was introduced into the chamber through a quartz window. The laser beam expanded to about 25 mm in diameter was emitted to the whole Al_2O_3 substrate ($15 \times 15 \times 2$ mm). TBCs are utilized with bond coats, usually Pt–Al or MCrAlY (M=Ni, Cr, etc.) alloys, to improve the adhesion to Ni-base alloy substrates. The bond coat is oxidized to form

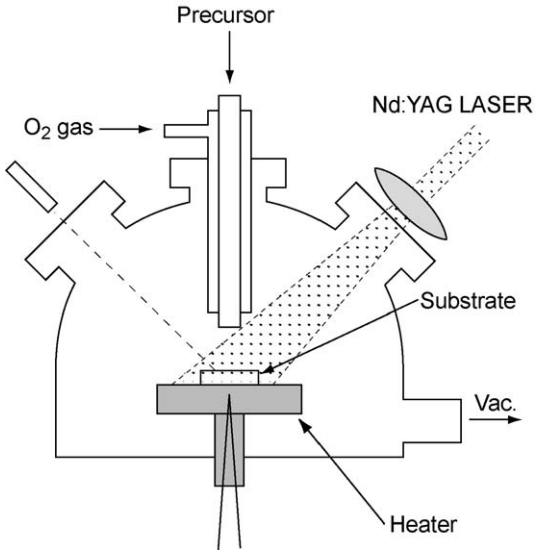

Fig. 1. A schematic diagram of LCVD apparatus.

Al_2O_3 surface layer in practical applications. Thus, in this study, Al_2O_3 substrates were used. The laser light intensity (I_L) was changed from 1.02×10^5 to 5.09×10^5 W/m^2. β-diketone complexes, $Zr(dpm)_4$ (dpm: dipivaloylmethanate) and $Y(dpm)_3$ were used for the preparation of YSZ films, and an alkoxide, $Ti(O\text{-}n\text{-}Bu)_4$ (Bu: C_4H_9), was used for the preparation of TiO_2 films. These precursors were heated at 473–573 K, and their vapors were carried by Ar gas into the chamber. Precursor fluxes of $Zr(dpm)_4$, $Y(dpm)_3$ and $Ti(O\text{-}n\text{-}Bu)_4$ were 1.2×10^{-6}, 0.3×10^{-7} to 1.0×10^{-7} and 4.9×10^{-5} mol/s, respectively. Although we have changed the Y_2O_3 content in YSZ films from 1 to 8 mol% by controlling the precursor temperature, the results of 4 mol% Y_2O_3 are described hereafter. O_2 gas was separately introduced by a double tube nozzle and mixed with the precursor vapors around the substrate. The substrate was pre-heated by the heater (Fig. 1). The pre-heating temperature (T_{pre}) means the temperature of substrate before laser irradiation. The substrate temperature (T_{sub}) was actually measured during deposition using a thermocouple (R-type) inserted in the substrate. The total pressure (P_{tot}) was kept at 0.93 kPa.

Surface and cross-sectional microstructures were observed by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was employed to investigate the nanostructure of films. The crystal structure and preferred orientation were determined by X-ray diffraction (XRD), and the composition was estimated by electron probe X-ray microanalysis (EPMA).

3. Results and discussion

3.1. Preparation of YSZ films

Fig. 2 demonstrates the effects of laser light intensity (I_L) and substrate pre-heating temperature (T_{pre}) on the deposition rates. While almost no deposition occurred below $I_L = 1.02 \times 10^5$ W/m^2, significant increase in deposition rates were observed above $I_L = 2.04 \times 10^5$ W/m^2. The deposition rates of YSZ films by thermal MOCVD have been commonly reported as few to several 10 μm/h; however, we have achieved a deposition rate of 108 μm/h by using cold-wall type CVD and the β-diketone precursors [8]. LCVD, on the other hand, has attained deposition rates more than several 100 μm/h. The deposition rate increased with increasing T_{pre} and I_L, and showed maximum at $I_L = 4.07 \times 10^5$ W/m^2 and $T_{pre} = 823$ K. The decrease in the deposition rate at higher T_{pre} could be resulted from the premature powder formation in a gas phase. A strong plasma emission was appeared and accompanied with the increase in deposition rates above a critical I_L. According to our plasma diagnosis, the plasma had an electron temperature of 4000 K with a continuous spectrum similar to the emission from a black body [11]. The substrate temperature (T_{sub}) increased in 150–200 K from pre-heating temperature after the laser irradiation. Since the laser power would have more capability to increase the T_{sub}, the laser might be partially reflected from the Al_2O_3 substrate surface resulting to rather small increase in T_{sub}. After the T_{sub} was stabilized, the