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**RAPID PUBLICATION**

# High Speed Deposition of $Y_2O_3$ Films by Laser-Assisted Chemical Vapor Deposition

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Thick yttria ($Y_2O_3$) films were synthesized at high speeds by laser-assisted chemical vapor deposition (LCVD) using an Y(dpm)$_3$ (dpm = dipivaloylmethanate) precursor. The effects of deposition conditions on the deposition rate and their microstructure were investigated. While the deposition rate was less than a few microns per hour at low laser powers ($P_L$) less than 100 W, significantly high deposition rates of more than 200 μm/h (56 nm/s) were obtained at $P_L$ more than 160 W. The highest deposition rate in this study was 300 μm/h (83 nm/s) being 100 to 1000 times greater than those of conventional CVD processes. Deposited films were dense and isotropic with no preferred orientation showing cauliflower-like microstructure.

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## 1. Introduction

Yttrium oxide ($Y_2O_3$) films have a wide variety of potential applications in electronic devices and hard coatings. In semiconductor processing, the components of plasma-etching apparatus (*e.g.*, liners, heater, electrostatic chuck, dome, etc.) can be coated with $Y_2O_3$ films as protection against corrosive high-density plasma source. These $Y_2O_3$-coated components therefore, have an excellent halogen plasma (commonly fluorine) corrosion resistance compared with non-coated ones because of the lower recombination rate of reactive plasma radicals for $Y_2O_3$.

Electron beam evaporation and chemical vapor deposition (CVD) methods have been employed to prepare $Y_2O_3$ films.[1–5,7,8] As-deposited films produced by electron beam evaporation were mainly amorphous and only transformed into crystalline phase upon annealing at moderate temperature. On the other hand, conventional CVD process has produced films with very low deposition rates in the range of around several μm/h, and therefore obtaining films with the desired thickness need a significantly long deposition time. For optimizing the materials performance against plasma-etching, considerably thick $Y_2O_3$ coatings are required. Thus, a new deposition process for thick $Y_2O_3$ coating has been desired to attain excellent microstructure control and high deposition rate.

We have reported that laser-assisted chemical vapor deposition (LCVD) can achieve extremely high deposition rate of 660 μm/h (180 nm/s) for yttria-stabilized zirconia (YSZ) films.[6] In this study, thick $Y_2O_3$ films were prepared by LCVD at high speeds and the effects of deposition conditions on the microstructure and the deposition rates were investigated.

## 2. Experimental

$Y_2O_3$ films were deposited by LCVD in a cold-wall semi-pancake-shaped chamber shown in Fig. 1. The Y(dpm)$_3$ (dpm = dipivaloylmethanate) solid precursor was evenly spread inside the porous aluminum crucible and inserted into the pre-heated crucible compartment. Y(dpm)$_3$ vapor and $O_2$ gas were each introduced into the chamber just above the substrate via the double nozzle to prevent premature reactions.

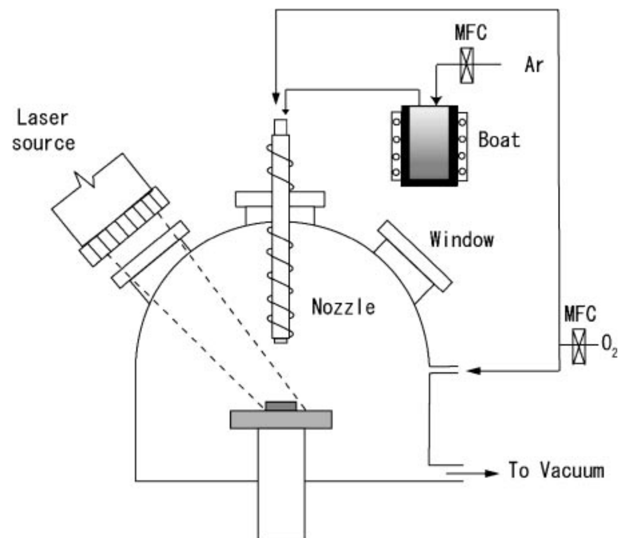


Fig. 1 Schematic diagram of the cold-wall type laser CVD chamber.

The sintered alumina substrates were cleansed with distilled water and ethanol then air-dried prior to deposition. Before starting the deposition, substrates were pre-heated at temperatures ($T_{pre}$) from R.T. up to 773 K. A continuous wave (CW) type Nd:YAG laser (Lee Laser 800 Series, $\lambda = 1063$ nm) was used with a spot size of about 15 mm in diameter which was enough to cover the entire substrate surface. For this study, the laser power intensity ($P_L$) used to irradiate the substrate was changed from 0–250 W. The total pressure was kept at 0.93 kPa by keeping the gas flow rates of $O_2$ ($FR_{O_2}$) at 200 cm$^3$/min ($3.3 \times 10^{-6}$ m$^3$/s) and Ar ($FR_{Ar}$) at 300 cm$^3$/min ($5 \times 10^{-6}$ m$^3$/s). These flow rates were controlled by mass-flow controllers (MFC's) connected in-line with each of the gas tubes. During deposition, the actual substrate deposition temperature ($T_{sub}$) was measured by an R-type thermocouple placed on the substrate holder. Table 1 summarizes the present experiment conditions. For this

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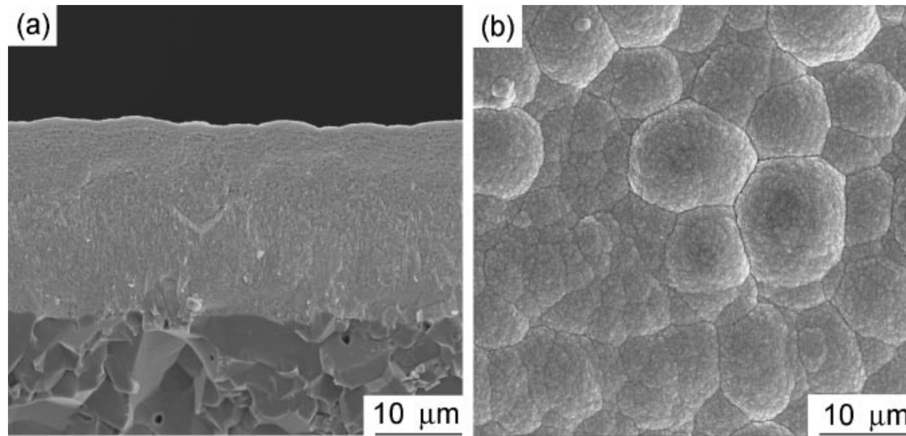


Fig. 2 Fractured cross-sectional (a) and surface (b) views of $Y_2O_3$ film prepared on an $Al_2O_3$ substrate ($T_{sub} = 973$ K, $P_L = 250$ W).

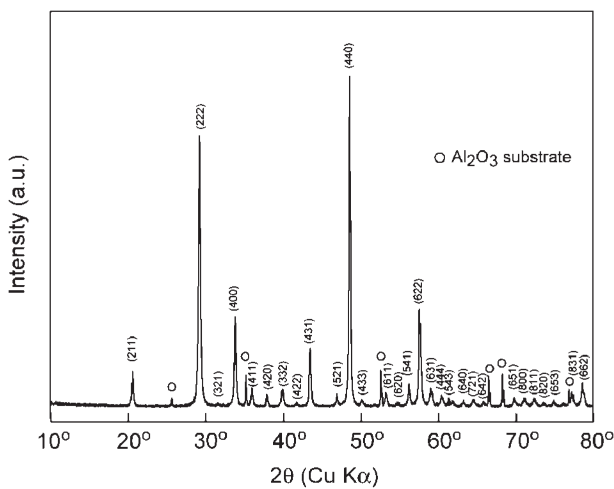


Fig. 3 Typical XRD pattern of $Y_2O_3$ films prepared at $T_{sub} = 973$ K and $P_L = 250$ W.

Table 1 Deposition conditions for LCVD of $Y_2O_3$ film.

| | |
|---|---|
| $Y(dpm)_3$ vaporization Temperature | 473 K |
| Substrate pre-heating Temperature ($T_{pre}$) | R.T.-773 K |
| Total Pressure ($P_{tot}$) | 0.93 kPa |
| Gas flowrates: | |
| Ar gas, (FR Ar) | $5.0 \times 10^{-6}$ m$^3$ s$^{-1}$ |
| $O_2$ gas, (FR $O_2$) | $3.3 \times 10^{-6}$ m$^3$ s$^{-1}$ |
| Laser Power ($P_L$) | 0-250 W |
| Substrate-Nozzle distance | 30 mm |

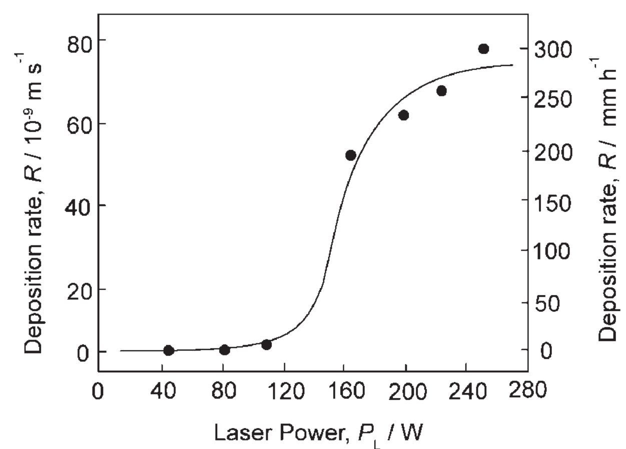


Fig. 4 Effect of laser power ($P_L$) on deposition rate ($T_{pre} = 773$ K).

deposition condition, deposited films had a maximum thickness of 25 μm (0–25000 nm).

Cross-section and surface morphology were investigated by scanning electron microscopy (SEM). The crystal structure and preferred orientation were analyzed by X-ray diffraction (XRD).

## 3. Results

The fractured cross-section and surface microstructure of the deposited $Y_2O_3$ film prepared at $T_{sub} = 973$ K and $P_L = 250$ W are shown in Fig. 2. The film exhibited good adhesion with the substrate. The as-deposited film was slightly gray in color particularly in the region where the gas nozzle was directly above the substrate. This could be attributed to the insufficient amount of source oxygen gas during deposition resulting in carbon impurity, then the film instantly changed to white upon heat treatment in air at around 973 K. Deposited films were dense for all $T_{pre}$ and $P_L$ conditions. The surface microstructure shown in Fig. 2(b) exhibits a cauliflower-like microstructure where the grain size increases with laser power.

The result of XRD is shown in Fig. 3 which corresponds to cubic $Y_2O_3$ according to JCPDS #83-0927. The film has a lattice constant of 1.0608 nm which is in agreement with the well-known cubic-C structure of $Y_2O_3$. No changes in the lattice parameter and preferred orientation were observed for films deposited at conditions stated in Table 1.

The relationship between the laser power ($P_L$) and deposition rate ($R$) at $T_{pre} = 773$ K is shown in Fig. 4. At $P_L < 100$ W, the deposition rate is low in the range of few microns per hour. At this low deposition rate, the increase in $T_{pre}$ does not significantly increase the deposition rate. At $P_L > 160$ W, the deposition rate is significantly increased to more than 200 μm/h (56 nm/s). This high deposition rate is closely associated with plasma formation during deposition. The plasma formation can be distinguished by the generation

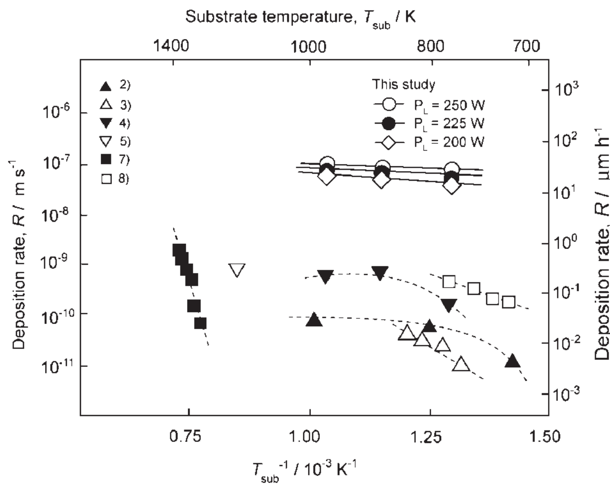


Fig. 5 Comparison of deposition rates for $Y_2O_3$ films between LCVD and conventional CVD at different pre-heating temperatures ($T_{pre}$).

of an intense light on the whole substrate immediately after an introduction of the carrier gas. The plasma was only observed at $P_L > 160$ W. Results of the plasma diagnosis using a single probe and emission spectroscopy in the case of YSZ films by LCVD were reported elsewhere.[6] The plasma caused a significant increase in the substrate deposition temperature ($T_{sub}$). Figure 5 demonstrates the deposition rate in the present study in the Arrhenius format compared with the literature data by conventional CVD. The deposition rates by the present LCVD were 100 to 1000 times higher than those reported by conventional CVD process. The highest deposition rate obtained in the present study was 300 μm/h (83 nm/s) at $T_{sub} = 973$ K and $P_L = 250$ W.

## 4. Discussion

The deposition mechanism in CVD can be discussed from the activation energy which is calculated from the gradient of lines in Fig. 5. A higher activation energy, usually more than several 10 kJ/mol, suggests a reaction-limited process. On the other hand, a lower activation energy commonly less than several kJ/mol, implies a diffusion-limited process. Since the deposition mechanism generally changes with increasing deposition temperature from a chemical reaction kinetic-limited process to a diffusion-limited process with accompanying increase in the deposition rates, the diffusion-limited process would be chosen in order to increase the deposition rate. The mean activation energy in the present LCVD was 5.7 kJ/mol, which is a characteristic of diffusion-limited process. Sipp *et al.* have deposited $Y_2O_3$ films by a hot-wall CVD using gaseous $YCl_3$–$CO_2$–$H_2$–Ar mixture.[7] Since $YCl_3$ is not reactive enough at low temperatures, the activation energy was very high (616 kJ/mol) suggesting a reaction-limited process at high temperatures around 1400 K. Brennfleck *et al.* have deposited $Y_2O_3$ films by a hot-wall type CVD using $Y(thd)_3$ and reported a deposition rate of 1.4 μm/h (0.38 nm/s) at 763 K.[8] A hot-wall type CVD reactor could often cause low deposition rates because precursor vapors were consumed by premature reactions in the gas phase and deposition reactions at the interior walls of CVD chamber. A cold-wall type CVD is usually advantageous to achieve high deposition rates due to insignificant deposition reactions in the gas phase and at the walls of the CVD chamber. Pulver *et al.* have achieved the highest deposition rate in cold wall chamber compared with that in the hot wall.[9] The present LCVD is classified as one of high deposition rate cold-wall CVD methods, which can be one of the reasons of its high deposition rate. The application of laser should obviously be the major reason of high deposition rate. The laser could only heat the substrate surface with negligible premature reactions in the gas phase. This well coincided with the result that the deposition efficiency was more than 80%. The plasma formation as above-mentioned could be strongly associated with the high deposition rate.

## 5. Conclusion

Dense $Y_2O_3$ films were deposited at high deposition rates on $Al_2O_3$ substrate by laser chemical vapor deposition at $P_{tot} = 0.93$ kPa. The film deposition rates significantly increased at more than a critical laser power. The high deposition rates of more than 200 μm/h (56 nm/s) were achieved at $P_L$ more than 160 W. The highest deposition rate was 300 μm/h (83 nm/s) at $T_{sub} = 973$ K and $P_L = 250$ W. The surface morphology showed cauliflower-like grains which increased with increasing $P_L$.

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