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Preparation of γ-Al_2O_3 films by laser chemical vapor deposition

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ABSTRACT

γ- and α-Al_2O_3 films were prepared by chemical vapor deposition using CO_2, Nd:YAG, and InGaAs lasers to investigate the effects of varying the laser wavelength and deposition conditions on the phase composition and microstructure. The CO_2 laser was found to mostly produce α-Al_2O_3 films, whereas the Nd:YAG and InGaAs lasers produced γ-Al_2O_3 films when used at a high total pressure. γ-Al_2O_3 films had a cauliflower-like structure, while the α-Al_2O_3 films had a dense and columnar structure. Of the three lasers, it was the Nd:YAG laser that interacted most with intermediate gas species. This promoted γ-Al_2O_3 nucleation in the gas phase at high total pressure, which explains the cauliflower-like structure of nanoparticles observed.

1. Introduction

The excellent chemical stability and mechanical properties of alumina (Al_2O_3) has seen it widely used as both a structural and refractory material. Chemical vapor deposition (CVD) has also been used to create films of the high-temperature alumina phase, α-Al_2O_3, which is widely used as a coating on cutting tools [1] due to its high hardness and thermal stability. Meanwhile, the low-temperature phase of Al_2O_3, γ-Al_2O_3, is best described as a defect spinel structure in which partly uncoordinated Al and O ions can act as acids and bases, respectively. This gives γ-Al_2O_3 a high catalytic activity [2], making Al_2O_3-supported catalysis more effective at high temperatures and high oxygen partial pressures that would destroy zeolite-based catalysts [3]. It also means that porous γ-Al_2O_3 films have great potential as a support material for catalysis and artificial photosynthesis [4].

Unfortunately, γ-Al_2O_3 films prepared at low deposition temperatures tend to have a low crystallinity and contain residual precursor phases [5], with Pflitsch et al. [6] reporting that γ-Al_2O_3 films have a surface morphology similar to amorphous Al_2O_3 films consisting of aluminum hydroxides. Nevertheless, Larsson et al. [7] have successfully prepared γ-Al_2O_3 films on a TiN buffer layer by using H_2S to promote the columnar growth of γ-Al_2O_3, but this also resulted in residual sulfur. Furthermore, as the films were prepared at low deposition temperatures, the deposition rates were only in the order of 0.3–0.4 $\mu m\,h^{-1}$.

We have previously argued that intense laser irradiation can enhance the CVD reaction [8–10], allowing highly oriented α-Al_2O_3 films to be produced at high deposition rates by using Nd:YAG and InGaAs lasers [11–13]. However, although high-powered lasers are known to significantly affect the CVD process, the effect of the laser's wavelength on the formation of γ- and α-Al_2O_3 phases in the film has not yet been elucidated. The present study therefore uses three different types of high-powered laser (*i.e.*, InGaAs, Nd:YAG, and CO_2 lasers) to explore their effects on the phase composition and microstructure of the Al_2O_3 film. This is herein discussed with a view to determining the precise mechanism and optimum conditions for growing γ-Al_2O_3 films by laser CVD.

2. Experimental procedures

A previously described laser CVD apparatus [11] was used to prepare Al_2O_3 films on yttria-stabilized zirconia (YSZ) substrates (5 mm × 5 mm × 1 mm) using aluminum acetylacetonate ($Al(acac)_3$) as the precursor. For this, a continuous-wave InGaAs (λ = 808 nm; 200 W max.), Nd:YAG (λ = 1064 nm; 240 W max.) or CO_2 (λ = 10.6 μm; 172 W max.) laser beam was introduced into the CVD chamber through a window to irradiate the entire substrate. A quartz window was used with the InGaAs and Nd:YAG lasers, while a ZnSe window was used for the CO_2 laser. In all cases, the substrate was preheated to 673 K on a hot stage.

The $Al(acac)_3$ was heated to its vaporization temperature of 453 K, and the resulting vapor was carried into the chamber by

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an Ar gas flow. A separate flow of O_2 gas was introduced into the chamber through a double-tube nozzle, though both gas flows were controlled to a rate of 1.6×10^{-7} m^3 s^{-1} to maintain a total pressure in the CVD chamber (P_{tot}) of 0.2–0.8 kPa. The deposition temperature (T_{dep}) was measured using a thermocouple inserted into a slot on the back side of the substrate. Once the temperature induced by the laser irradiation stabilized, deposition was conducted for 0.6 ks.

The phase composition of each of the films produced was determined by X-ray diffraction (XRD; Rigaku RAD-2C). The surface and cross-sectional microstructure was observed by a scanning electron microscope (SEM; Hitachi S-3100H) and transmission electron microscope (TEM; Topcon EM-002B). The deposition rate (R_{dep}) was calculated from the film's thickness and deposition time.

3. Results and discussion

3.1. Preparation of Al_2O_3 films using a CO_2 laser

Fig. 1 shows the XRD patterns obtained from the Al_2O_3 films prepared using the CO_2 laser, in which we see that α-Al_2O_3 films were obtained at T_{dep} = 837–1240 K and P_{tot} = 0.2–0.8 kPa (Fig. 1(a)), whereas a γ-Al_2O_3 film with a small amount of α-Al_2O_3 was obtained at T_{dep} = 833 K and P_{tot} = 0.2 kPa (Fig. 1(b)). From the typical SEM images of these films, it is evident that although the α-Al_2O_3 film has a dense cross-sectional structure with polygonal facets on the surface (Fig. 2(a) and (b)), the γ-Al_2O_3 film has more of a cauliflower-like structure made of fine grains (Fig. 2(c) and (d)).

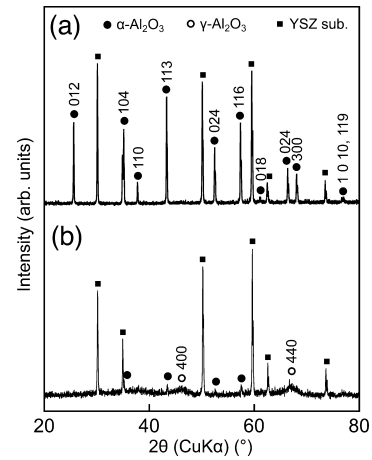

Fig. 1. XRD patterns of Al_2O_3 films prepared using a CO_2 laser at P_{tot} = 0.2 kPa and T_{dep} of (a) 896 K and (b) 833 K.

In Fig. 3, the effects of varying T_{dep} and P_{tot} on the phase composition and microstructure of Al_2O_3 films prepared using the CO_2 laser can be seen in the distinction between the dual phase γ-Al_2O_3 film with α-Al_2O_3 (half-filled circles) and single-phase α-Al_2O_3 film (filled circles). Note that the formation of γ-Al_2O_3 was independent of P_{tot}, and that a single-phase γ-Al_2O_3 film was not obtained with the CO_2 laser.

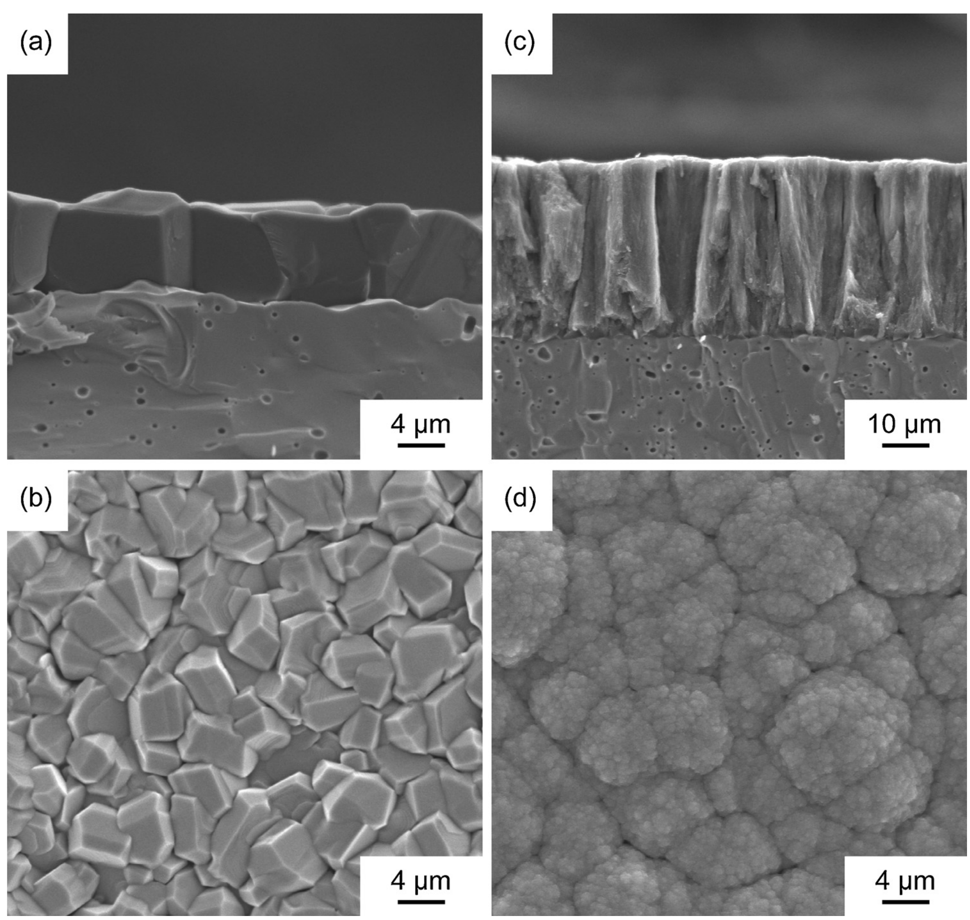

Fig. 2. SEM images showing the (a, c) cross-section and (b, d) surface of Al_2O_3 films prepared using a CO_2 laser: (a, b) α-Al_2O_3 film prepared at P_{tot} = 0.2 kPa and T_{dep} = 1140 K; (c, d) γ-Al_2O_3 film with a small amount of α-Al_2O_3 prepared at P_{tot} = 0.2 kPa and T_{dep} = 833 K.