Effect of Precursor Supply on (100) and (001) Orientations of α -Al₂O₃ Film Prepared by Laser CVD

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Abstract. α -Al₂O₃ films were prepared by laser chemical vapor deposition and the effects of precursor evaporation temperature (T_{vap}) and oxygen gas flow rate (FR_0) on phase and orientation of Al₂O₃ films were investigated. At $T_{vap} = 413$ K, (100)-oriented α -Al₂O₃ and θ -Al₂O₃ were codeposited. The amount of θ -Al₂O₃ increased with increasing FR_0 . At $T_{vap} = 433-443$ K, α -Al₂O₃ films showed a (001) orientation. (100)- and (001)-oriented α -Al₂O₃ films had a rectangular- and hexagonal-shaped grains, respectively, and showed a columnar in cross section. Grain size of (100)- and (001)-oriented α -Al₂O₃ films decreased from 10 to 2 µm with increasing FR_0 from 0.085 to 0.85 Pa m³ s⁻¹. Deposition rate increased from 100 to 300 µm h⁻¹ with increasing T_{vap} from 413 to 443 K.

Introduction

Since α -alumina (α -Al₂O₃) has high thermal and chemical stability, low thermal conductivity and excellent high-temperature hardness, α -Al₂O₃ coating has much attention as a protective coating for cemented carbide (WC-Co/Ni) cutting tools to improve its mechano-thermal properties and lifetime [1]. α -Al₂O₃ coating would enable Ti(C,N)-based cermet cutting tools to expand wide applications. Orientation and microstructural control of α -Al₂O₃ coating is highly demanded to develop high performance cutting tools [2]. α -Al₂O₃ coating has been commonly prepared by thermal chemical vapor deposition (CVD) [3]; however, the deposition temperature is usually more than 1300 K, which is too high to coat cutting tools, and orientation and microstructure is hardly controlled. We have developed a new CVD route using high-power lasers (laser CVD) for preparing various thick films with controlling nano- and macro-structures [4–6]. In laser CVD process, chemical reactions are significantly accelerated around a substrate, enabling low temperature and high-speed deposition with orientation control.

In the present study, α -Al₂O₃ films were prepared by laser chemical vapor deposition and the effects of precursor evaporation temperature (T_{vap}) and oxygen gas flow rate (FR_O) on the orientation of α -Al₂O₃ films was investigated.

Experimental procedure

A schematic of laser CVD apparatus has been reported elsewhere [7]. Aluminum acetylacetonate (Al(acac)₃) was used as a precursor. Al(acac)₃ was heated at $T_{\text{vap}} = 413-443$ K and its vapor was carried into a chamber with Ar gas (0.34 Pa m³ s⁻¹). O₂ gas was separately introduced into the chamber through a double-tube nozzle. Flow rate of O₂ gas changed from $FR_0 = 0.085$ to 0.85 Pa m³ s⁻¹. The total pressure in the chamber was held at 0.9 kPa. Yttria-stabilized zirconia (YSZ) plate (12.5 mm × 12.5 mm × 1 mm) was used as a substrate. The substrate was heated on a hot stage at a preheating temperature 873 K, and a thermocouple was inserted backside of the substrate to measure the deposition temperature (T_{dep}). A continuous-wave mode Nd:YAG laser beam (wavelength: 1064 nm; diameter: 20 mm; output 192 W) was introduced through a quartz window to irradiate the whole substrate.

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The crystal phase was analyzed by X-ray diffraction (XRD, Rigaku RAD-2C) using Cu Kα X-ray radiation. The surface and cross-sectional morphology was observed by a scanning electron microscope (SEM, Hitachi S-3100H).

Results and discussion

Figure 1 shows the XRD pattern of the Al₂O₃ films prepared on YSZ substrate at $FR_0 = 0.17$ Pa m³ s⁻¹ and various T_{vap} . At $T_{\text{vap}} = 413 \text{ K}$, (100)-oriented α -Al₂O₃ film were obtained and θ -Al₂O₃ was codeposited with (100)-oriented α -Al₂O₃ (Fig. 1(a)). At $T_{\text{vap}} = 433$ K, single-phase (001)-oriented α -Al₂O₃ film was prepared (Fig. 1(b)). The diffraction intensity of the (006) plane is only 2 compared with 100 for the (104) plane according to the JCPDS #46-1212, and the diffraction peak of the (006) peak cannot be identified in common α -Al₂O₃. Therefore, the XRD pattern with a small (006) peak implied significant (001) orientation of the α -Al₂O₃.

Figure 2 summarizes the phase and orientation relation at various FR_0 and T_{vap} . At $T_{\text{vap}} = 413$ K, α -Al₂O₃ films had a (100) orientation, while θ -Al₂O₃ was codeposited with α -Al₂O₃ and the amount of θ -Al₂O₃ increased with increasing FR_0 from 0.085 to 0.85 Pa m³ s⁻¹. Single-phase θ -Al₂O₃ film was obtained at $FR_0 = 0.85$ Pa m³ s⁻¹. At $T_{\text{vap}} = 423$ K, α -Al₂O₃ films has no orientation independent of FR_0 . At $T_{\text{vap}} = 433-443$ K, (001)-oriented α -Al₂O₃ films were prepared.

Figure 3 shows the surface and cross-sectional microstructure of the α -Al₂O₃ films prepared at $FR_0 = 0.17$ and 8.5 Pa m³ s⁻¹, and $T_{vap} = 413$ and 433 K. (100)-oriented α -Al₂O₃ film prepared at T_{vap} = 413 K and $FR_0 = 0.17$ Pa m³ s⁻¹ ($T_{dep} =$ 1143 K) had a rectangular shaped grains (Fig. 3(a)). A hexagonal facet inclined to substrate surface was also observed. Rectangular and hexagonal facets could correspond α -Al₂O₃ {100} or {110} planes and α-Al₂O₃ (001) plane, respectively. At $FR_0 = 8.5 \text{ Pa m}^3 \text{ s}^{-1}$ ($T_{dep} = 1210 \text{ K}$), the shape of grain became fine and granular (Fig. 3(b)). (001)-oriented α -Al₂O₃ films showed a columnar growth in cross section (Fig. 3(a')).



Fig. 1 XRD patterns of Al₂O₃ films prepared on YSZ substrate at $FR_0 = 0.17$ Pa m³ s⁻¹ and $T_{vap} = 413$ (a) and 433 (b) K.



Fig. 2 XRD patterns of Al₂O₃ films prepared on YSZ substrate at $FR_0 = 0.17$ Pa m³ s⁻¹ and $T_{vap} = 413$ (a) and 433 (b) K. Open and closed circles indicate (001)- and non-oriented α -Al₂O₃ films, respectively. Open squares and triangles indicate (100)-oriented α -Al₂O₃ films with θ -Al₂O₃ and θ -Al₂O₃ films, respectively.

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(001)-oriented α -Al₂O₃ film prepared at $T_{\text{vap}} = 433$ K and $FR_0 = 0.17$ Pa m³ s⁻¹ ($T_{\text{dep}} = 1199$ K) had a hexagonal terrace (Fig. 3(c)). Hexagonal terraces grew parallel to substrate surface can be associated with α -Al₂O₃ (001) plane. With increasing FR_0 from 0.085 to 0.85 Pa m³ s⁻¹, the size of hexagonal grain of (001)-oriented α -Al₂O₃ films decreased from 10 to 2 µm. (001)-oriented α -Al₂O₃ film also showed a columnar growth in cross section and the columnar grains were characterized by a feather-like structure (Fig. 3(c')). Deposition rate increased from 100 to 300 µm h⁻¹ with increasing T_{vap} from 413 to 443 K.



Fig. 3 Surface (a-d) and cross-sectional (a', c') SEM images of (100)-oriented α -Al₂O₃ films prepared at $T_{\text{vap}} = 413$ K and $FR_0 = 0.17$ (a) and 0.85 (b) Pa m³ s⁻¹, and (001)-oriented α -Al₂O₃ films prepared at $T_{\text{vap}} = 443$ K and $FR_0 = 0.17$ (c) and 0.85 (d) Pa m³ s⁻¹.

Summary

 α -Al₂O₃ films were prepared on YSZ substrate at various T_{vap} and FR_0 . (100)-oriented α -Al₂O₃ films were obtained at $T_{\text{vap}} = 413$ K. θ -Al₂O₃ was codeposited with (100)-oriented α -Al₂O₃ and the amount of θ -Al₂O₃ increased with increasing FR_0 from 0.085 to 0.85 Pa m³ s⁻¹. α -Al₂O₃ films has no orientation at $T_{\text{vap}} = 423$ K. At $T_{\text{vap}} = 433-443$ K, (001)-oriented α -Al₂O₃ films were prepared. (100)- and (001)-oriented α -Al₂O₃ films had a rectangular- and hexagonal-shaped grains, respectively, and showed a columnar growth in cross section. Grain size of (100)- and (001)-oriented α -Al₂O₃ films decreased from 10 to 2 μ m with increasing FR_0 from 0.085 to 0.85 Pa m³ s⁻¹. Deposition rate increased from 100 to 300 μ m h⁻¹ with increasing T_{vap} from 413 to 443 K.

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