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Low-temperature deposition of α-Al_2O_3 films by laser chemical vapor deposition using a diode laser

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ABSTRACT

We prepared Al_2O_3 films by laser chemical vapor deposition (LCVD) using a diode laser and aluminum acetylacetonate ($Al(acac)_3$) precursors and investigated the effects of laser power (P_L), deposition temperature (T_{dep}), and total pressure (P_{tot}) in a reaction chamber on the crystal phase, microstructure, and deposition rate (R_{dep}). An amorphous phase was obtained at P_L = 50 W, whereas an α-phase was obtained at P_L > 100 W. At P_L = 150 and 200 W (1 0 4)- and (0 1 2)-oriented α-Al_2O_3 films were obtained, respectively. The R_{dep} of α-Al_2O_3 films increases with decreasing P_L and P_{tot}. Single-phase α-Al_2O_3 film was obtained at T_{dep} = 928 K, which is about 350 K lower than that obtained by conventional thermal CVD using $Al(acac)_3$ precursor.

1. Introduction

Alumina crystallizes in many polymorphs such as α-, γ-, θ-, and κ-Al_2O_3. Metastable polymorphs, such as γ, θ and κ transform to α-Al_2O_3 at temperatures above 1273 K. Thus, the stable α-Al_2O_3 films are preferred when used as a top layer on Ti(C, N) coated cemented carbide cutting tools intended to be used in high-speed cutting [1–3].

To date, Al_2O_3 films have been prepared by various processes, such as physical vapor deposition (PVD) [4], chemical vapor deposition (CVD) [1–3,5], and the sol–gel method [6]. CVD using $AlCl_3$–CO_2–H_2 as a precursor has been a common commercial method for the preparation of α-Al_2O_3 films [7]. However, by-products such as HCl may corrode the deposition chamber; moreover, a high deposition temperature, usually ranging from 1200 to 1300 K, may degrade the mechanical properties of the substrates.

Moderate-temperature deposition has been used for Ti(C, N)/Al_2O_3 multilayer coatings [8]; however, κ-Al_2O_3 was easily co-deposited and transformed to α-Al_2O_3 during the cutting process, leading to cracking of the films due to volume contraction encountered in the κ to α transformation [9]. Therefore, it is of importance to develop new low-temperature processes for deposition of α-Al_2O_3 films.

Extensive work has been devoted to reduce the deposition temperature of CVD Al_2O_3 films using metal–organic precursors (MOCVD) and plasma enhancement (PECVD) [10–13]. Although MOCVD has an advantage in the preparation of crystalline Al_2O_3 films at low-temperature, it tends to deliver the γ and κ phases. These metastable phases transform into the α phase at high temperature, causing the abrasion of Al_2O_3 films [13]. Furthermore, the co-deposition of an amorphous phase was often reported at low-temperature. However, no report has yet appeared addressing the low-temperature deposition of α-Al_2O_3 in a single-phase by MOCVD. Although PECVD has efficiently decreased the deposition temperature of α-Al_2O_3 [10], reduced pressure and low precursor concentration (to maintain plasma formation) leads to low deposition rates for the films [14,15].

Lasers have been applied to CVD mainly to enhance the reactivity of precursors by an incident laser beam parallel or vertical to the substrate surface [16,17]. Photon-controlled chemical reactions of precursors in laser CVD (LCVD) would lead to low-temperature deposition. We have employed a high-power (~250 W at most) continuous-wave Nd:YAG laser to heat substrates and simultaneously activate precursors emitted onto a wide-area substrate (~15 mm × 15 mm) and have prepared ZrO_2 and TiO_2 films at low-temperature with high deposition rates [18,19]. We have also prepared single-phase α-Al_2O_3 films at moderate-temperature of 1100 K and high deposition rate of 250 μm h^{-1} by LCVD using an Nd:YAG laser [20]. Since a diode laser has higher photon energy than an Nd:YAG laser, a lower deposition temperature would be expected by using a diode laser in conjunction with CVD.

In the present study, we demonstrate low-temperature deposition of α-Al_2O_3 films by LCVD with a diode laser and investigate the effects of deposition conditions on the crystal phase, microstructure, and deposition rate of α-Al_2O_3 films.

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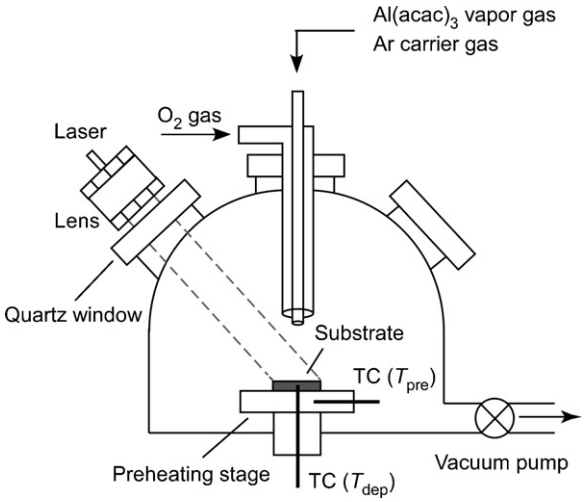

Fig. 1. Schematic of the LCVD apparatus.

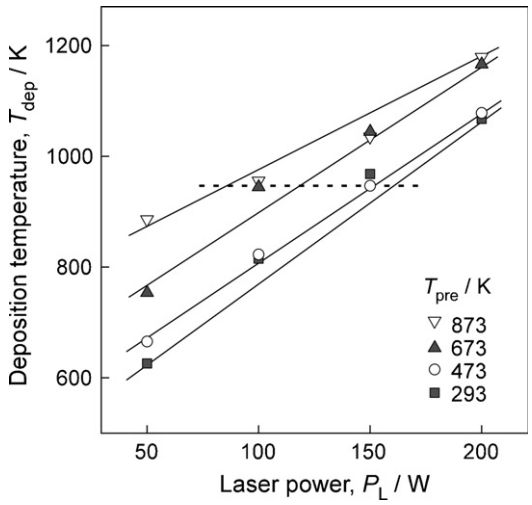

Fig. 2. Deposition temperature of Al_2O_3 films as a function of T_{pre} and P_L at P_{tot} = 0.2 kPa and T_{Al} = 443 K.

2. Experimental

A vertical, cold-wall type CVD apparatus was constructed to prepare Al_2O_3 films. Fig. 1 shows a schematic of the LCVD apparatus. AlN plates (10 mm × 10 mm × 1 mm) were used as substrates. These were preheated on a heating stage using an electrical heater with a preheating temperature (T_{pre}) ranging from 293 to 873 K, after which the entire substrate was irradiated by an InGaAlAs diode laser (wavelength: 808 nm). The laser beam was introduced into the chamber through a quartz-glass window and was slightly expanded by a lens to about 20 mm in diameter at the substrate surface. The laser was operated in continuous mode with power P_L ranging from 50 to 200 W. A thermocouple (TC) was inserted into a slot in the substrate to measure the deposition temperature (T_{dep}). $Al(acac)_3$ (99%) precursor was evaporated by heating, its vapor being transported into the chamber using Ar gas (99.99%). The $Al(acac)_3$ precursor vaporization temperature (T_{Al}) was varied from 443 to 503 K. O_2 gas (99.9995%) was introduced into the chamber separately through a double-tube nozzle to react with $Al(acac)_3$. The Ar and O_2 gas flow rates were set at 8.25×10^{-7} and 1.65×10^{-6} m^3 s^{-1}, respectively. The total pressure (P_{tot}) in the CVD chamber was controlled between 0.2 and 1.6 kPa. The feed pipes and the nozzle were heated at 523 K to prevent condensation of the precursor vapor. Table 1 summarizes the deposition parameters for preparing Al_2O_3 films.

The crystal phases were examined by X-ray diffraction (θ–2θ scan) with Cu Kα radiation (XRD; Rigaku, RAD-2C). The morphology and thickness were characterized using a scanning electron microscope (SEM; Hitachi, S-3100H) and the deposition rate (R_{dep}) was calculated from the thickness and deposition time.

Table 1
Deposition conditions of Al_2O_3 films by LCVD.

Laser power, P_L	50–200 W
Substrate preheating temperature, T_{pre}	293–873 K
Total pressure in chamber, P_{tot}	0.2–1.6 kPa
$Al(acac)_3$ precursor temperature, T_{Al}	443–503 K
Gas line and nozzle temperature	523 K
Flow rate of $Al(acac)_3$ carrier gas (Ar)	8.25×10^{-7} m^3 s^{-1}
Flow rate of O_2 gas	1.65×10^{-6} m^3 s^{-1}
Distance between nozzle and substrate	25 mm

3. Results and discussion

3.1. The phase composition of Al_2O_3

The T_{dep} was determined primarily by a combination of P_L and T_{pre}. Fig. 2 shows the relationship between T_{dep} and P_L for different values of T_{pre} at T_{Al} = 443 K and P_{tot} = 0.2 kPa. The T_{dep} increases with increasing P_L and T_{pre}.

Fig. 3 shows XRD patterns of Al_2O_3 films prepared at T_{Al} = 443 K, P_{tot} = 0.2 kPa, and P_L = 50–200 W. No peaks except that of the substrate were identified at P_L = 50 W (Fig. 3(a)). At P_L = 100 W and T_{dep} = 825 K, the XRD peaks were indexed as α- and γ-Al_2O_3 (Fig. 3(b)). Single-phase α-Al_2O_3 film was obtained at P_L = 120 W and T_{dep} = 928 K (Fig. 3(c)). The peaks of α-Al_2O_3 film became stronger and showed a (1 0 4) orientation at P_L = 150 W (Fig. 3(d)). At P_L = 200 W (0 1 2)-oriented α-Al_2O_3 film was significantly obtained (Fig. 3(e)).

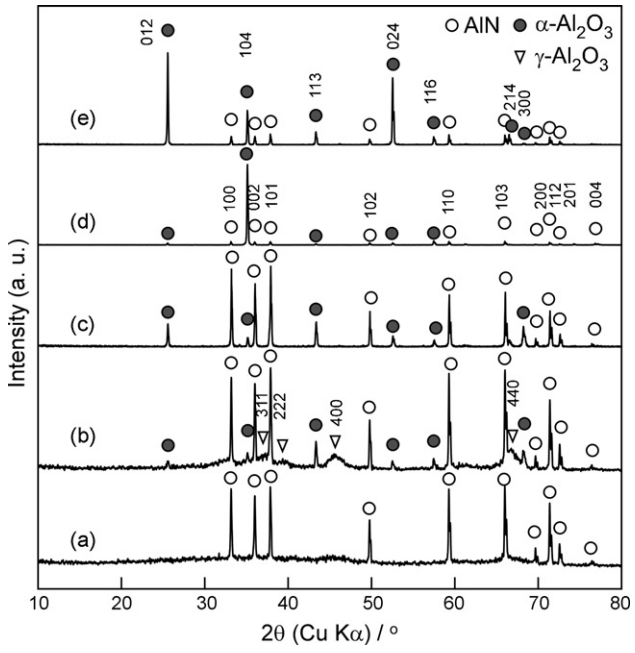

Fig. 3. XRD patterns of Al_2O_3 films prepared at T_{pre} = 293 K, T_{Al} = 443 K, and P_{tot} = 0.2 kPa: (a) P_L = 50 W and T_{dep} = 623 K, (b) P_L = 100 W and T_{dep} = 825 K, (c) P_L = 120 W and T_{dep} = 928 K, (d) P_L = 150 W and T_{dep} = 973 K, and (e) P_L = 200 W and T_{dep} = 1077 K.