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# Preparation of Hydroxyapatite and Calcium Phosphate Films by MOCVD

Mitsutaka Sato<sup>1</sup>, Rong Tu<sup>2</sup> and Takashi Goto<sup>2</sup>

<sup>1</sup>Department of Materials Science, Graduate School, Tohoku University, Sendai 980-8577, Japan

<sup>2</sup>Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Ca-P-O films were prepared by MOCVD using Ca(dpm)<sub>2</sub> and (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>PO precursors. The crystal phase changed with changing deposition conditions of substrate temperature ( $T_{\text{sub}}$ ), total pressure ( $P_{\text{tot}}$ ) and molar ratio of Ca and P precursors ( $R_{\text{Ca/P}}$ ).  $\alpha$ -tricalcium phosphate ( $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) in a single phase was obtained at  $T_{\text{sub}} = 973$  K,  $R_{\text{Ca/P}} < 0.3$  and  $T_{\text{sub}} = 1073$  K,  $R_{\text{Ca/P}} = 0.1$  to 0.5. Hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) in a single phase was first prepared by MOCVD at  $T_{\text{sub}} = 973$  K,  $R_{\text{Ca/P}} = 0.5$  and  $T_{\text{sub}} = 1073$  K,  $R_{\text{Ca/P}} = 0.8$  to 1. The maximum deposition rate of  $\alpha$ -TCP and HAp films in a single phase were 6.0 and 4.0 nm s<sup>-1</sup> at  $P_{\text{tot}} = 0.8$  kPa and  $T_{\text{sub}} = 1073$  K, respectively. [doi:10.2320/matertrans.MRA2007145]

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**Keywords:** metal-organic chemical vapor deposition, calcium phosphate, crystal structure, microstructure, deposition rate

## 1. Introduction

Titanium and its alloy have been widely used as artificial implants in a medical field because of their good biocompatibility and mechanical properties.<sup>1,2</sup> It is known that the reproduction of bones on Ti implants can be promoted by bioceramic coatings such as hydroxyapatite (HAp, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>),  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP,  $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>),  $\beta$ -tricalcium phosphate ( $\beta$ -TCP,  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) and calcium titanate (CaTiO<sub>3</sub>).<sup>3</sup> Many studies on these coatings by sputtering,<sup>4,5</sup> sol-gel,<sup>6,7</sup> plasma spray deposition,<sup>8,9</sup> have been conducted to improve the biocompatibility of Ti substrates.

Although chemical vapor deposition (CVD) is an advantageous coating process due to relatively high deposition rates with good morphology controllability and well-adherence to substrates as indicated in TiO<sub>2</sub><sup>10</sup> and ZrO<sub>2</sub><sup>11</sup> coatings. A few reports on the preparation of Ca-P-O films by CVD has been published.<sup>12,13</sup> Allen *et al.* prepared  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> pyrochlore film at 1123 K using Ca(dpm)<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> precursors by a hot-wall type CVD.<sup>12</sup> The pyrochlore films were heat-treated at 1373 to 1623 K and then  $\beta$ -TCP films were obtained. Darr *et al.* prepared fluorine-containing carbonated hydroxyapatite films by CVD.<sup>13</sup> However, detailed deposition conditions have not been reported in these reports, and no studies have succeeded to prepare HAp,  $\alpha$ -TCP and  $\beta$ -TCP films in a single phase.

In this study, Ca-P-O films were prepared by CVD and the effects of deposition conditions on phases, morphology, preferred crystal orientation and deposition rate were investigated.

## 2. Experimental Procedure

Ca-P-O films were prepared by a vertical cold-wall type CVD apparatus.<sup>14</sup> Ca(dpm)<sub>2</sub> (bis-dipivaloylmethanato-calcium) and (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>PO (triphenylphosphate) source powders were heated at 523 to 573 and 493 to 533 K, respectively. Their vapors were carried into the CVD reactor with Ar carrier gas. O<sub>2</sub> gas was separately introduced by using a double tube nozzle, and mixed with the precursor vapors in a

mixing chamber placed above the substrate holder. The total gas flow rate ( $FR_{\text{tot}} = FR_{\text{Ar}} + FR_{\text{O}_2} + FR_{\text{source vapor}}$ ) was fixed at  $3.33 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . The total pressure ( $P_{\text{tot}}$ ) in the CVD reactor was changed from 0.2 to 0.8 kPa. The substrate temperature ( $T_{\text{sub}}$ ) was controlled between 873 and 1073 K. Fused quartz glass plates of  $10 \times 15 \times 0.5$  mm were used as substrates due to the convenience to identify the crystal phase and to observe the cross-section of films. Furthermore, alumina plate was used as substrate in the case of peel-off of film on glass substrate due to the thermal expansion mismatch.

The deposition conditions are summarized in Table 1. The crystal structure was analyzed by X-ray diffraction (XRD). Fourier transform infrared spectroscopy (FT-IR) was employed to evaluate the O-H bond of HAp. The microstructure and thickness were examined by scanning electron microscopy (SEM). The deposition rate ( $R_{\text{dep}}$ ) was determined from the relationship between thickness and deposition time.

## 3. Results and Discussion

### 3.1 Crystal structure

Figure 1 shows the relationship between precursor temperature ( $T_{\text{prec}}$ ) and the evaporation rate of Ca(dpm)<sub>2</sub> and (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>PO. The evaporation rates exponentially increased

Table 1 Deposition conditions of Ca-P-O films.

Precursor Temperature, $T_{\text{prec}}$	
Ca(dpm) <sub>2</sub>	: 533 to 573 K
(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> PO	: 493 to 533 K
Total gas flow rate, $FR_{\text{tot}}$	: $3.33 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Carrier Gas	: Ar
Ca(dpm) <sub>2</sub>	: $0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> PO	: $0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
O <sub>2</sub> gas flow rate, $FR_{\text{O}_2}$	: 0.17 to $1.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Total pressure, $P_{\text{tot}}$	: 0.2 to 1.0 kPa
Deposition temperature, $T_{\text{sub}}$	: 873 to 1123 K
Deposition time	: 0.9 ks
Substrate	: quartz glass, alumina

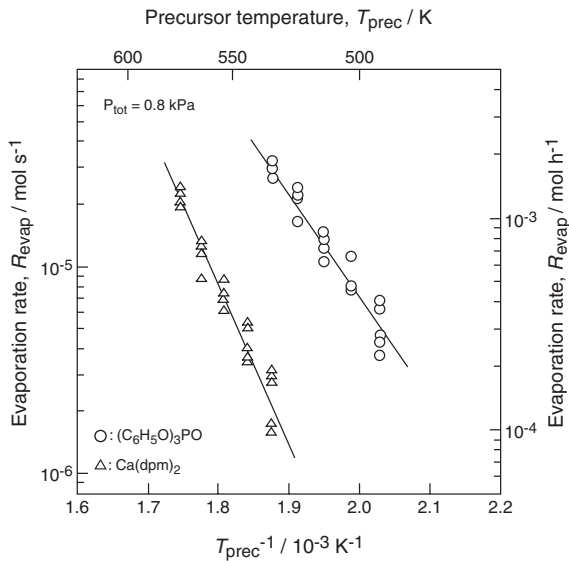


Fig. 1 Effect of precursor temperature on the evaporation rate of  $\text{Ca}(\text{dpm})_2$  and  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$  at  $P_{\text{O}_2} = 0.32$  kPa and  $P_{\text{tot}} = 0.8$  kPa.

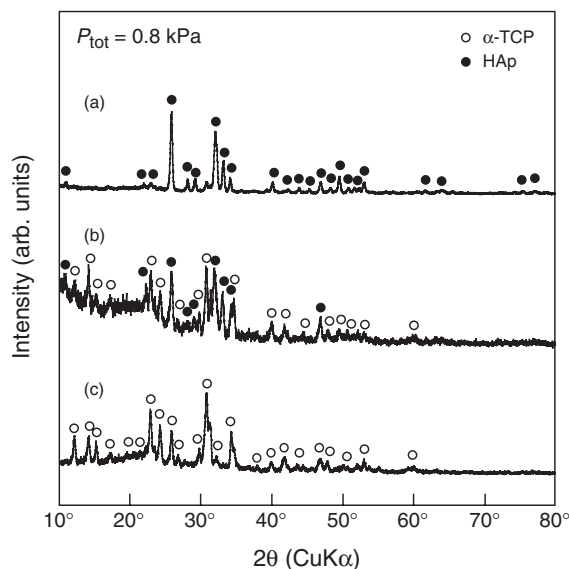


Fig. 2 XRD patterns of Ca-P-O films prepared at  $P_{\text{O}_2} = 0.32$  kPa,  $P_{\text{tot}} = 0.8$  kPa,  $T_{\text{sub}} = 1073$  K and  $R_{\text{Ca}/\text{P}} = 0.84$  (a), 0.60 (b), 0.24 (c).

with  $T_{\text{prec}}$ . Although the evaporation rate of  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$  was 10 times greater than that of  $\text{Ca}(\text{dpm})_2$ , the precursor molar ratio of Ca to P ( $R_{\text{Ca}/\text{P}}$ ) was precisely controlled by changing the  $T_{\text{prec}}$ .

Figure 2 shows X-ray diffraction patterns of Ca-P-O films prepared at  $T_{\text{sub}} = 1073$  K and  $P_{\text{tot}} = 0.8$  kPa.  $\alpha$ -TCP and HAp films in a single phase were obtained at  $R_{\text{Ca}/\text{P}} = 0.24$  ( $T_{\text{prec}}(\text{Ca}) = 553$  K and  $T_{\text{prec}}(\text{P}) = 533$  K) and 0.84 ( $T_{\text{prec}}(\text{Ca}) = 563$  K and  $T_{\text{prec}}(\text{P}) = 513$  K), respectively. A mixture film of  $\alpha$ -TCP and HAp was prepared at  $R_{\text{Ca}/\text{P}} = 0.6$ . The HAp phase had a preferred orientation of (002) at  $2\theta = 25.9^\circ$ .

Figure 3 shows the FT-IR spectrum of the HAp film in a single phase. The adsorption bands due to  $\text{PO}_4^{3-}$  and O-H stretching bonds of HAp were observed at 1100 and 3600  $\text{cm}^{-1}$ , respectively. It is well understood that HAp would lose

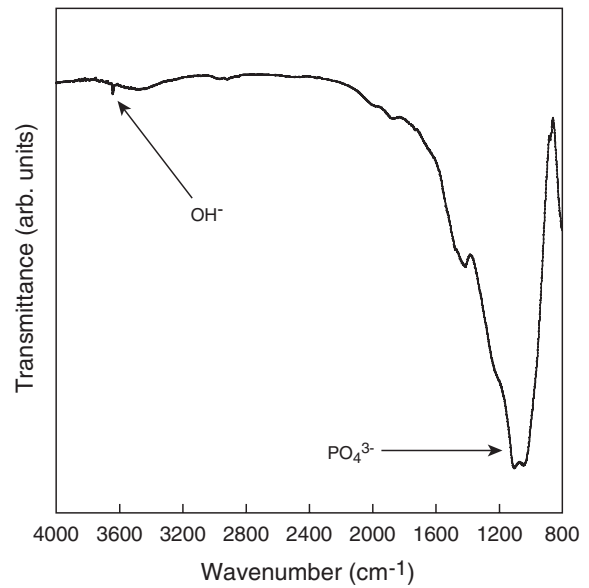


Fig. 3 FT-IR spectrum of HAp film prepared at  $P_{\text{O}_2} = 0.32$  kPa,  $P_{\text{tot}} = 0.8$  kPa  $T_{\text{sub}} = 1073$  K and  $R_{\text{Ca}/\text{P}} = 0.84$ .

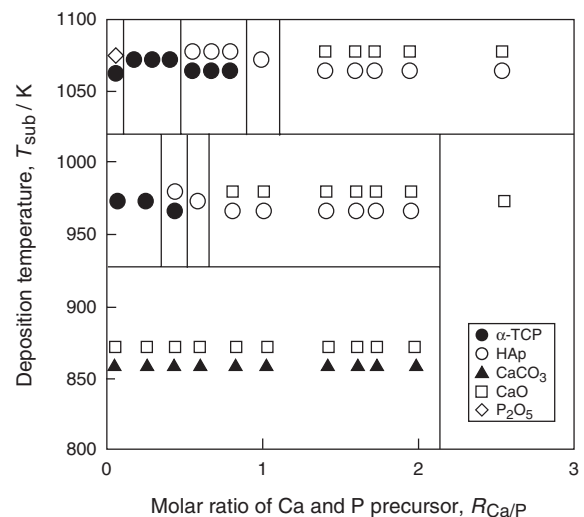


Fig. 4 CVD formation diagram of Ca-P-O films at  $P_{\text{O}_2} = 0.32$  kPa and  $P_{\text{tot}} = 0.8$  kPa.

an OH group at high temperature, and may transform to oxyhydroxyapatite (OHAp,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x$ ,  $\square$ : defect,  $x < 1$ ) or oxyapatite (OAp,  $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ ).<sup>15-18</sup> OHAp and OAp were often obtained by sputtering and sintering because of high vacuum atmosphere and high temperature.<sup>4</sup>) In this study, the formation of HAp was confirmed by the O-H stretching bond. The peak intensity of the O-H bond of HAp was almost the same as that in a HAp film prepared by a sol-gel method.<sup>19,20</sup>

Figure 4 presents a CVD formation diagram of Ca-P-O films as functions of  $T_{\text{sub}}$  and  $R_{\text{Ca}/\text{P}}$  at  $P_{\text{tot}} = 0.8$  kPa. At  $T_{\text{sub}} = 873$  K, no calcium phosphate phase was obtained. The films were a mixture of  $\text{CaCO}_3$  and CaO at  $R_{\text{Ca}/\text{P}} < 2$  and CaO in a single phase at  $R_{\text{Ca}/\text{P}} > 2$ . At  $T_{\text{sub}} = 973$  K,  $\alpha$ -TCP and HAp films in a single phase were obtained at  $R_{\text{Ca}/\text{P}} < 0.3$  and  $0.5 < R_{\text{Ca}/\text{P}} < 0.6$ , respectively. The film were a mixture of  $\alpha$ -TCP and HAp at  $0.3 < R_{\text{Ca}/\text{P}} < 0.5$ . The films were a

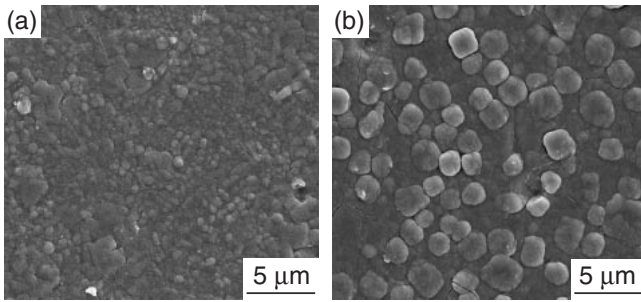


Fig. 5 Effect of  $P_{O_2}$  on the surface morphology of Ca-P-O films prepared at  $T_{sub} = 1073$  K,  $P_{tot} = 0.8$  kPa and  $R_{Ca/P} = 0.13$ .  $P_{O_2} = 0.08$  (a),  $0.36$  kPa (b).

mixture of HAp and CaO at  $0.6 < R_{Ca/P} < 2.1$  and were CaO in a single phase at  $R_{Ca/P} > 2.1$ . At  $T_{sub} = 1073$  K,  $\alpha$ -TCP film in a single phase was obtained at  $0.1 < R_{Ca/P} < 0.4$ , and HAp film in a single phase was obtained at  $0.8 < R_{Ca/P} < 1.0$ . At  $R_{Ca/P} < 0.1$ , the film was a mixture of  $\alpha$ -TCP and  $P_2O_5$ . A mixture of  $\alpha$ -TCP and HAp were prepared at  $0.4 < R_{Ca/P} < 0.8$ . A mixture of HAp and CaO were prepared at  $R_{Ca/P} > 1.0$ . In the present study, CaO-rich and  $P_2O_5$ -rich phase tend to form at low and high  $T_{sub}$ , respectively. Although stoichiometrical  $R_{Ca/P}$  in  $\alpha$ -TCP and HAp are 1.5 and 1.67, respectively, the films in a single phase were obtained at lower  $R_{Ca/P}$ . This may be caused by homogeneous nucleation in gas atmosphere, incomplete decomposition of precursor and/or formation of by-product. In the CVD phase diagram of Ca-Ti-O system,  $CaTiO_3$  in a single phase formed at  $0.8 < R_{Ca/Ti} < 1.02$ .<sup>21)</sup> The  $R_{Ca/Ti}$  was lower than the stoichiometrical ratio of 1 in  $CaTiO_3$ , consistent with the results in this study. In addition, CaO-rich and  $TiO_2$ -rich phase was reported to be easily formed at low and high  $T_{sub}$  in Ca-Ti-O system, respectively,<sup>21)</sup> showing almost same trend with Ca-P-O system.

### 3.2 Microstructure

Figure 5 shows the effect of  $P_{O_2}$  on the surface morphology of Ca-P-O films prepared at  $T_{sub} = 1073$  K,  $R_{Ca/P} = 0.13$  ( $T_{prec} (Ca) = 543$  K and  $T_{prec} (P) = 533$  K) and  $P_{tot} = 0.8$  kPa. Both films were  $\alpha$ -TCP almost in a single phase containing a small amount of HAp and showed a (510) orientation of  $\alpha$ -TCP. The films had a granular microstructure. The grain size was less than  $1 \mu m$  at  $P_{O_2} = 0.08$  kPa (Fig. 5(a)) and increased to about  $3 \mu m$  at  $P_{O_2} = 0.32$  kPa (Fig. 5(b)). The thickness of the films was  $0.4 \mu m$  at  $P_{O_2} = 0.08$  kPa and  $1.8 \mu m$  at  $P_{O_2} = 0.32$  kPa. Therefore, it is suggested that the growth of film was promoted at high  $P_{O_2}$  because of enough quantum of oxygen for crystal growth.

Figure 6 depicts the effect of  $T_{sub}$  on the surface and cross-sectional morphologies of  $\alpha$ -TCP films in a single phase prepared at  $R_{Ca/P} = 0.27$  ( $T_{prec} (Ca) = 583$  K and  $T_{prec} (P) = 583$  K),  $P_{tot} = 0.8$  kPa and  $P_{O_2} = 0.32$  kPa. The  $\alpha$ -TCP film prepared at  $T_{sub} = 973$  K had a dense microstructure, and the grain size was about  $0.5 \mu m$  (Figs. 6(a) and (b)), showing an orientation of (510). The  $\alpha$ -TCP film prepared at  $T_{sub} = 1073$  K also had a dense granular microstructure. The grain size was about  $2 \mu m$  in length (Figs. 6(c) and (d)), showing a (510) orientation as demonstrated in Fig. 7(a).

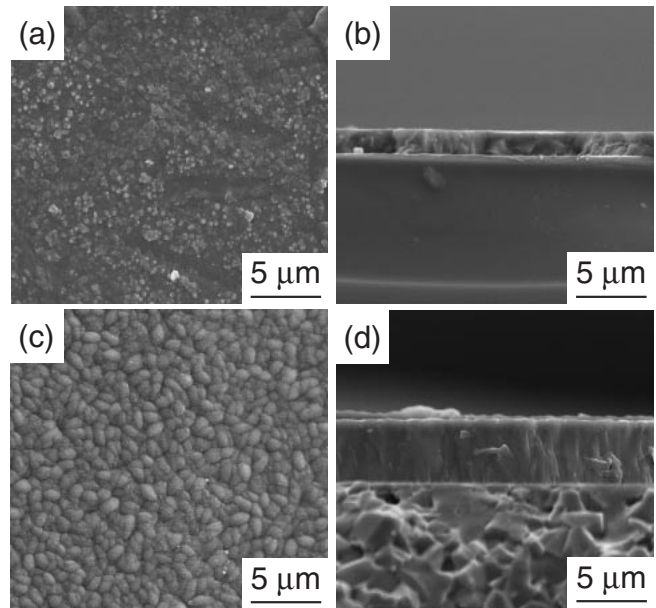


Fig. 6 Effect of  $T_{sub}$  on the surface and cross-sectional morphologies of  $\alpha$ -TCP films prepared at  $P_{O_2} = 0.32$  kPa and  $P_{tot} = 0.8$  kPa. (a), (b)  $T_{sub} = 973$  K and  $R_{Ca/P} = 0.26$ , (c), (d)  $T_{sub} = 1073$  K and  $R_{Ca/P} = 0.27$ .

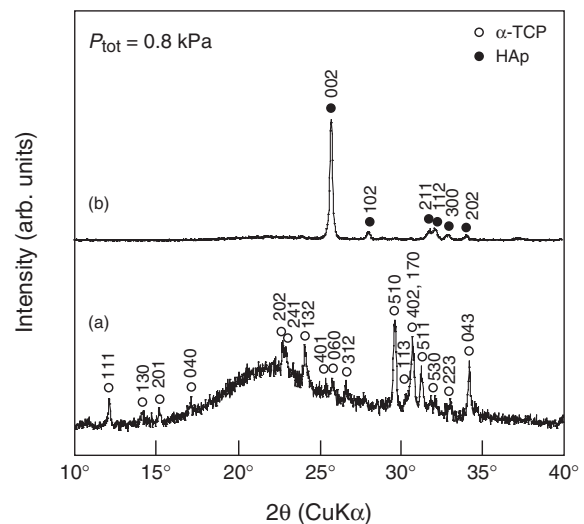


Fig. 7 XRD patterns of (510)-orientated  $\alpha$ -TCP (a) and (002)-orientated HAp (b) films prepared at  $T_{sub} = 1073$  K,  $P_{tot} = 0.8$  kPa and  $P_{O_2} = 0.32$  kPa.

Figure 8 depicts the effect of  $T_{sub}$  on the surface and cross-sectional morphologies of HAp films in a single phase prepared at  $P_{tot} = 0.8$  kPa and  $P_{O_2} = 0.32$  kPa. The HAp film prepared at  $T_{sub} = 973$  K ( $T_{prec} (Ca) = 543$  K and  $T_{prec} (P) = 503$  K) had a dense and fine microstructure with a grain size of about  $0.2 \mu m$  (Figs. 8(a) and (b)). The HAp film prepared at  $T_{sub} = 1073$  K ( $T_{prec} (Ca) = 563$  K and  $T_{prec} (P) = 513$  K) had a dense and columnar microstructure with a coarser grain size of about  $1$  to  $2 \mu m$  (Figs. 8(c) and (d)), while these grains consisted of smaller grains about  $0.2 \mu m$  in diameter. With increasing  $T_{sub}$ , the mobility of chemical species on the substrate surface increased, resulting in the growth of grain size. Both HAp films had a significant preferred (002) orientation as demonstrated in Fig. 7(b).

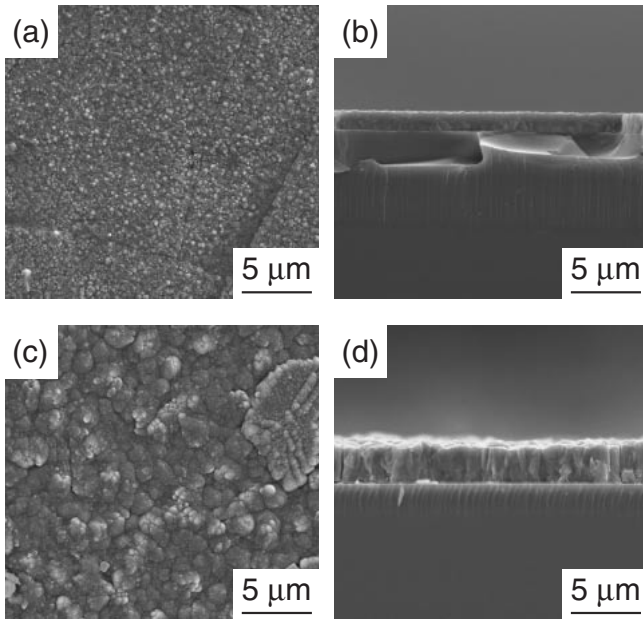


Fig. 8 Effect of  $T_{\text{sub}}$  on the surface and cross-sectional morphologies of HAp films prepared at  $P_{\text{O}_2} = 0.32$  kPa and  $P_{\text{tot}} = 0.8$  kPa. (a), (b)  $T_{\text{sub}} = 973$  K and  $R_{\text{Ca/P}} = 0.55$ . (c), (d)  $T_{\text{sub}} = 1073$  K and  $R_{\text{Ca/P}} = 0.84$ .

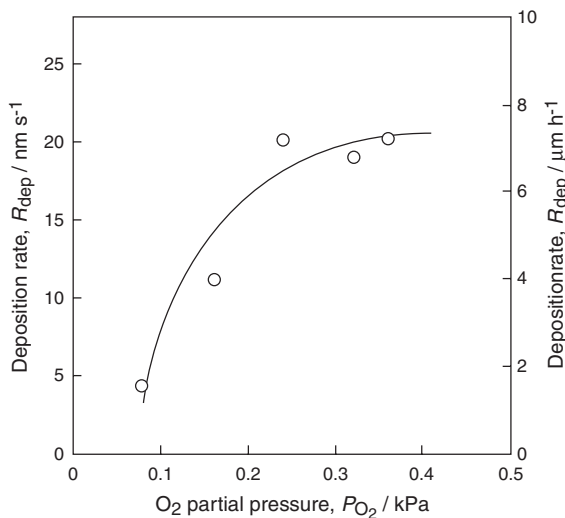


Fig. 9 Effect of  $P_{\text{O}_2}$  on the deposition rate at  $T_{\text{sub}} = 1073$  K and  $P_{\text{tot}} = 0.8$  kPa ( $\text{Ca}(\text{dpm})_2$ :  $T_{\text{prec}} = 543$  K,  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ :  $T_{\text{prec}} = 533$  K).

In the Ca-Ti-O system, the surface and cross-sectional morphology of  $\text{CaTiO}_3$  film changed from dense to columnar structure with increasing  $T_{\text{sub}}$ . The  $\text{CaTiO}_3$  film having a cauliflower-like complicated surface morphology and columnar structure showed a good adhesion with substrate.<sup>21)</sup> On the other hand, Ca-P-O film showed a dense and smooth microstructure at any deposition condition. However, Ca-P-O film with a columnar structure and more complicated surface morphology may be obtained by further increment of  $T_{\text{sub}}$  and/or concentration of source precursor of Ca and P.

### 3.3 Deposition rate

Figure 9 depicts the effect of oxygen partial pressure ( $P_{\text{O}_2}$ ) on the deposition rate ( $R_{\text{dep}}$ ) at  $T_{\text{sub}} = 1073$  K,  $P_{\text{tot}} = 0.8$  kPa and  $R_{\text{Ca/P}} = 0.2$  ( $T_{\text{prec}}(\text{Ca}) = 543$  K and  $T_{\text{prec}}(\text{P}) = 533$  K).

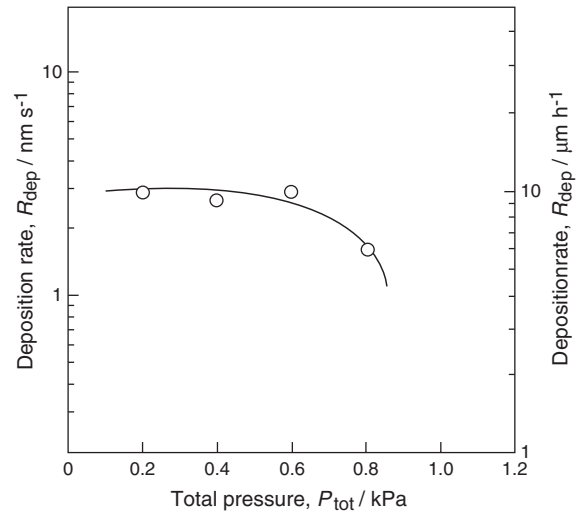


Fig. 10 Effect of  $P_{\text{tot}}$  on the deposition rate at  $P_{\text{O}_2} = 0.32$  kPa and  $T_{\text{sub}} = 1073$  K. ( $\text{Ca}(\text{dpm})_2$ :  $T_{\text{prec}} = 543$  K,  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ :  $T_{\text{prec}} = 533$  K).

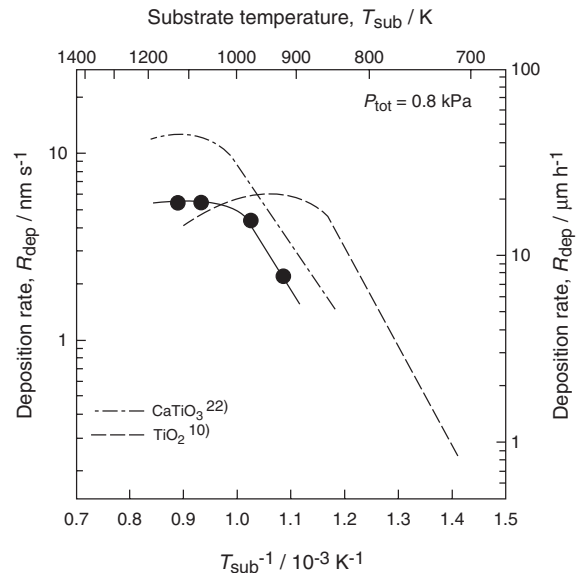


Fig. 11 Effect of  $T_{\text{sub}}$  on the deposition rate at  $P_{\text{O}_2} = 0.32$  kPa and  $P_{\text{tot}} = 0.8$  kPa. ( $\text{Ca}(\text{dpm})_2$ :  $T_{\text{prec}} = 543$  K,  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ :  $T_{\text{prec}} = 533$  K).

At  $P_{\text{O}_2} < 0.25$  kPa, the  $R_{\text{dep}}$  increased with increasing  $P_{\text{O}_2}$ , and almost saturated at  $P_{\text{O}_2} > 0.25$  kPa. This increment of  $R_{\text{dep}}$  may be caused by the promotion of decomposition of source precursor by increasing of  $P_{\text{O}_2}$ . This result suggests that the driving force of film deposition may be influenced by not only the supersaturation degree of source precursor but also the concentration of oxygen.

Figure 10 shows the effect of  $P_{\text{tot}}$  on the  $R_{\text{dep}}$  of Ca-P-O films at  $T_{\text{sub}} = 1073$  K and  $R_{\text{Ca/P}} = 0.2$  ( $T_{\text{prec}}(\text{Ca}) = 543$  K and  $T_{\text{prec}}(\text{P}) = 533$  K). The  $R_{\text{dep}}$  was almost constant at  $P_{\text{tot}} < 0.6$  kPa and slightly decreased at  $P_{\text{tot}} = 0.8$  kPa. It is commonly observed in CVD that the deposition rate decreases at a high  $P_{\text{tot}}$  mainly due to premature chemical reaction in a gas phase.<sup>22)</sup>

Figure 11 shows the relationship between  $T_{\text{sub}}$  and  $R_{\text{dep}}$  at  $R_{\text{Ca/P}} = 0.25$  ( $T_{\text{prec}}(\text{Ca}) = 583$  K and  $T_{\text{prec}}(\text{P}) = 583$  K) and  $P_{\text{O}_2} = 0.32$  kPa in the Arrhenius format. The  $R_{\text{dep}}$  increased

with increasing  $T_{\text{sub}}$ , and showed a maximum value of 6.0 and 4.0  $\text{nm s}^{-1}$  for  $\alpha$ -TCP and HAp at  $T_{\text{sub}} = 1073$  K, respectively. This  $R_{\text{dep}}$  is about 10 times greater than that of usual sputtering.<sup>4)</sup> With further increasing of  $T_{\text{sub}}$ , the  $R_{\text{dep}}$  slightly increased. It is known that the rate-controlling step in CVD can be a diffusion-limited process in a high  $T_{\text{sub}}$  region with an activation energy ( $E_a$ ) of a few  $\text{kJ mol}^{-1}$  and a chemical reaction limited process in a low  $T_{\text{sub}}$  region with the  $E_a$  of more than several  $10 \text{ kJ mol}^{-1}$ . Since no literature data on the deposition rate of Ca-P-O films by CVD was available, our results of  $\text{CaTiO}_3$ <sup>21)</sup> and  $\text{TiO}_2$ <sup>10)</sup> films by CVD were compared in Fig. 11. The  $R_{\text{dep}}$  of Ca-P-O films showed almost similar trend as those of  $\text{CaTiO}_3$  and  $\text{TiO}_2$  films. The  $E_a$  of  $\text{CaTiO}_3$  and  $\text{TiO}_2$  films were 70 and 100  $\text{kJ mol}^{-1}$ , implying the rate-controlling step of a chemical reaction. The  $E_a$  of 80  $\text{kJ mol}^{-1}$  in the present study can also suggest a chemical reaction limited process in the low  $T_{\text{sub}}$  region.

#### 4. Conclusions

Ca-P-O films were prepared by MOCVD using  $\text{Ca}(\text{dpm})_2$  and  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$  precursors. At  $T_{\text{sub}} = 973$  to 1073 K,  $\alpha$ -TCP and HAp films in a single phase were obtained by controlling mainly  $R_{\text{Ca/P}}$  and  $T_{\text{sub}}$ . HAp films had a significant (002) orientation, and  $\alpha$ -TCP films showed (510) orientations at  $T_{\text{sub}} = 973$  and 1073 K. The surface of  $\alpha$ -TCP and HAp films were dense and granular microstructure. The grain size of HAp film (about 0.2  $\mu\text{m}$ ) was much smaller than that of  $\alpha$ -TCP (2 to 3  $\mu\text{m}$ ). The deposition rate of Ca-P-O films increased with increasing  $P_{\text{O}_2}$  and  $T_{\text{sub}}$ , and increased with decreasing  $P_{\text{tot}}$ . The highest deposition rate of  $\alpha$ -TCP film was 6.0  $\text{nm s}^{-1}$  and that of HAp film was 4.0  $\text{nm s}^{-1}$  at  $T_{\text{sub}} = 1073$  K,  $P_{\text{tot}} = 0.8$  kPa and  $P_{\text{O}_2} = 0.32$  kPa.

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