Characteristics of Calcium Phosphate Films Prepared by Pulsed Laser Deposition under Various Water Vapor Pressures

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Calcium phosphate films were prepared by using a pulsed laser deposition (PLD) technique with a KrF excimer laser (248 nm, 2 J/cm^2) under a wide range of H_2O pressures at a substrate temperature of 600 °C. Sintered hydroxyapatite (HA) was used as the target. The background H_2O pressure during deposition critically affected the density and the composition of the deposited films. With increasing H_2O pressure, the growth rate increased, and the mass deposited was almost constant. Consequently, the density gradually decreased with H_2O pressure, resulting in a porous microstructure under 0.37 Torr. The Ca/P ratio of the film decreased with H_2O pressure, and the crystal structure of the deposited film changed in accordance with the Ca/P ratio. The observed peaks were from hydroxyapatite (Ca/P = 1.67) for H_2O pressures above 0.13 Torr, and the peaks from high Ca/P phases, such as tetracalcium phosphate [$Ca_4O(PO_4)_2$, Ca/P = 2] and CaO (Ca/P = ∞), were observed for the film deposited at 0.02 Torr. A high-density hydroxyapatite film with a high degree of crystallinity was obtained under a H_2O pressure of 0.25 Torr.

I. INTRODUCTION

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HA), has been widely used as a biomaterial for many applications in both dentistry and orthopedics because it is chemically similar to the mineral component of bones and tooth minerals in mammals [1,2]. Nevertheless, due to the poor mechanical properties of bulk HA, it cannot be used as an implant-device material for load-bearing applications. The solution is to apply HA as a coating on Ti or Ti-based alloy implants [3,4]. In this way, the mechanical properties of the implants are supported by the metallic structure while the osteointegration is promoted by the bioactive surface of HA. To date, plasma-spray (PS) [5] is the only commercially available technique for coating implants with HA, and the PS coated implants exhibit faster bone healing than uncoated implants [2,6]. However, there were some issues affecting the long-term stability of the implants. The main problems of PS coatings are related with low crystallinity, the presence of other calcium phosphate phases, the porosity, and the poor coating-substrate adhesion [6–8]. High temperature and fast cooling during PS coating produce a mixture of vari-

ous calcium phosphates. Most of the calcium phosphates are bioactive. However, except for the dense crystalline HA, they exhibit a fast dissolution rate in body fluids [9, 10]. Furthermore, the adhesion of PS coatings to metallic implants is often not sufficient in clinic applications. We also should consider that the adhesion strength of PS coatings reported in the literature can be overestimated because the adhesives used for tensile tests can penetrate into the interface between the coating and the implant through the pores of the coating [11].

As an alternative method for HA deposition, pulsed laser deposition (PLD) has been investigated to produce thin HA films with high crystallinity and adhesion. PLD is one of the most flexible methods for depositing complex multielemental oxides [12–16]. It was reported that crystalline HA thin films can be produced using ultraviolet lasers, such as KrF [17,18], ArF [18–20], or Nd : YAG [21,22]. Substrate temperatures over 400 °C are required to obtain crystalline film, and reactive ambient gases containing water vapor (H_2O) are essential to depositing HA films. Many research efforts have been mainly focused on the influence of the deposition parameters on the crystal structure of the deposited film. There have been works on studying the effect of H_2O pressure, particularly on the crystal structures and the chemical compositions of

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the deposited film. Arias *et al.* reported that a minimum H_2O pressure of 0.23 Torr was necessary to deposit a crystalline film using an ArF excimer laser and that the films were less crystalline again at pressures above 0.6 Torr [19,20]. For the Nd : YAG laser (266 or 355 nm) case, Zeng and Lacefield reported that the films had different Ca/P ratios from that of pure HA targets, which assured the presence of non-HA phases [21]. Fernández-Pradas *et al.* reported that Ca-rich phases were obtained at 0.075 Torr while HA is obtained at 0.34 Torr with some alpha tricalcium phosphate (α-TCP) [22]. There has been no report on the influence of H_2O pressure for pulsed KrF-laser deposition of calcium phosphate films.

In this work, calcium phosphate films were deposited using a pulsed KrF excimer laser from pure HA targets under wide range of H_2O pressures, and the crystal structure and the Ca/P ratio of the deposited films were examined. The deposition rate, the deposition rate, the density, and the surface morphology of the deposited film were also investigated.

II. EXPERIMENT

Sintered HA discs were used as targets for PLD. The HA powder was cold-isostatic pressed at 170 MPa and then sintered in air at 1220 °C for 2 h at a heating rate of 0.5 °C/min. The resulting density of the target was 2.94 g/cm^3, which is about 94 % of the theoretical density of HA. The average Ca/P ratios of the disc before and after sintering were 1.71 and 1.84, respectively. X-ray diffraction (XRD) spectrum obtained after sintering showed strong peaks from HA and very small peaks from other calcium phosphates.

Calcium phosphate films were deposited in a vacuum chamber by utilizing a pulsed KrF laser (TuiLaser ThinFilmStar 20) operating at a repetition rate of 20 Hz with a wavelength of 248 nm. The laser beam was focused on a rotating target at an angle of 45 °C. The fluence and the number of shots were fixed at 2 J/cm^2 and 36,000, respectively. The films were deposited at a substrate temperature of 600 °C with various pressures of H_2O inside the chamber. The H_2O pressure was controlled in the range from 0.01 to 1.0 Torr by adjusting a metering valve between the vacuum chamber and an ampoule filled with deionized water. A Si wafer with 100-nm-thick thermal oxide layer on it was used as the substrate, and the calcium phosphate film was deposited exclusively on a circular area with a diameter of 10 mm by utilizing a shadow mask.

The thickness of the deposited film was determined by using cross-sectional scanning electron microscopy (X-SEM). In considering the spatial distribution of the film thickness, the film thickness was measured at more than 10 positions over the entire deposited area for each sample. The mass of the sample was measured before and after deposition in order to obtain the mass of the deposited film. X-ray diffraction was used to investigate the

phase composition of the films, and energy dispersive X-ray spectroscopy (EDX) was used to measure the atomic concentrations of the elements composing the film, such as Ca, P and O. The surface morphology of the films was observed using a scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

Fig. 1 shows the growth rate of the film as a function of H_2O pressure at a laser fluence of 2 J/cm^2. The growth rate slightly decreased with increasing H_2O pressure from 0.02 Torr to 0.07 Torr and then continuously increased with additional increases in the H_2O pressure. However, the mass of the deposited film did not vary as
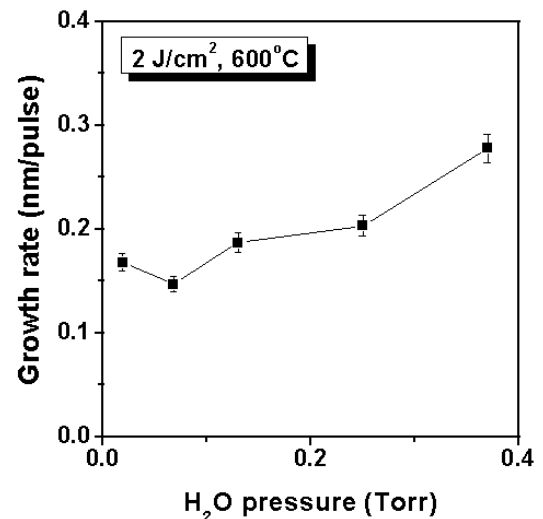

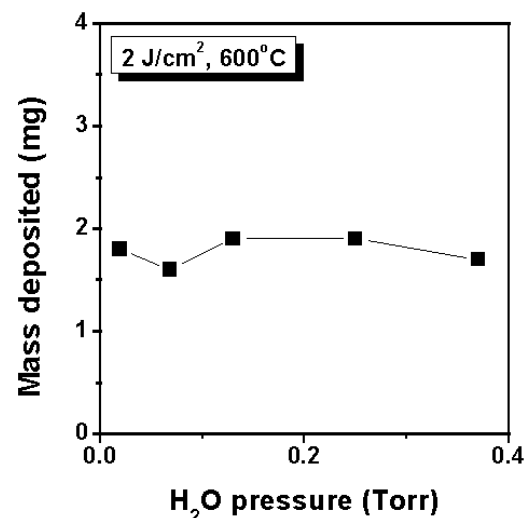Fig. 1. Growth rate of the film as a function of H_2O pressure at 600 °C with a laser fluence of 2 J/cm^2.

Fig. 2. Mass of the film as a function of H_2O pressure at 600 °C with a laser fluence of 2 J/cm^2. The number of shots was fixed at 3.6×10^4.
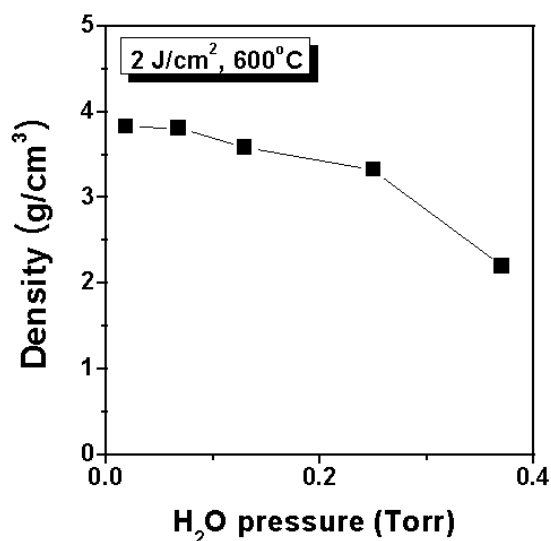
Fig. 3. Density of the film as a function of H_2O pressure at 600 °C with a laser fluence of 2 J/cm^2.

Fig. 4. Surface morphologies of the films deposited at 600 °C under various H_2O pressures with a laser fluence of 2 J/cm^2.

much as the film thickness, as shown in Fig. 2, which means that the total amount of material delivered from the target to the substrate was almost constant over a wide range of H_2O pressures. Therefore, the change in the deposition rate is thought to be due to the change in the film density with increasing H_2O pressure. The density of the film was calculated from the mass and the volume of the deposited film, and the volume was obtained by multiplying the average film thickness by the deposited area. Fig. 3 shows that the density of film gradually decreased with increasing H_2O pressure. The density of the film was higher than that of bulk HA (3.15 g/cm^3) under H_2O pressures below 0.25 Torr while the density was approximately 70 % of that of bulk HA under a H_2O pressure of 0.37 Torr.

Fig. 4 shows the surface morphologies of the films deposited under various H_2O pressures. At a low H_2O pressure of 0.02 Torr, the film consisted of a smooth matrix and granular particles. The grain structure started to evolve with increasing pressure. The microstructure eventually became porous at the grain boundaries under a H_2O pressure of 0.37 Torr, which agrees well with the low film density in Fig. 3.

In the PLD process, the deposition flux is so energetic that the particles have kinetic energies comparable to the bond strengths in the growing film. The energies of the depositing species promote surface diffusion on the growing film, resulting in high-quality films at lower substrate temperatures as compared with other thermal deposition techniques [12]. However, high-energy tails can result in implantation into the film and produce a significant disruption of the film crystallinity. In addition, it has shown that particles with energies above 50 eV can cause material to be resputtered from the film surface [13]. This not only reduces the effective deposition rate but can also lead to a change in the stoichiometry of multielemental
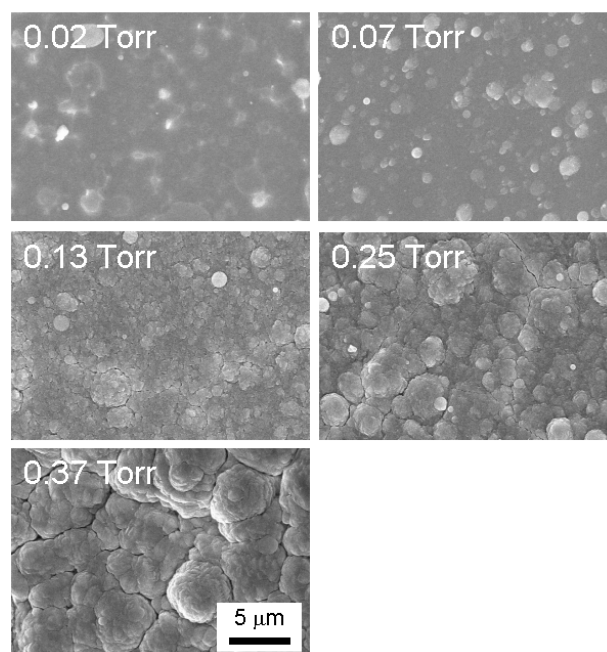
films by preferential resputtering. By introducing a background gas, such as H_2O in the present work, the entire kinetic-energy distribution can be shifted to lower values [23]. Consequently, implantation, as well as resputtering, will be reduced as the background gas pressure is increased. However, the increased background gas pressure will cause scattering of the plume with the gas, as well. The deposition rate can increase due to the reduced resputtering or can decrease due to a less-directed plume. In the present work, however, the influences of these factors seemed to be balanced by each other because the deposited mass was almost constant over a wide range of H_2O pressures. We will discuss more details later.

On the other hand, the film density is also affected by the energy of the deposition flux. The densification of the film due to implantations of high-energy deposition flux might be an origin of the high-density film deposited under a low H_2O pressure. As the H_2O pressure is increased, the quenching effect of the background gas will reduce surface diffusion of the depositing species under high H_2O pressures, resulting in a decrease in the film density, as in Fig. 3. These results confirmed that a depositing flux with a sufficient kinetic energy is required to obtain high-density films.

The chemical composition and the constituting phases of the films were analyzed using the EDX and the XRD techniques. Fig. 5 shows the Ca/P ratios of the films determined by using EDX. The Ca/P ratio gradually decreased from 2.5 to 1.8 with increasing H_2O pressure. Fig. 6 shows the XRD patterns obtained from the deposited films. At a H_2O pressure of 0.02 Torr, the diffrac-
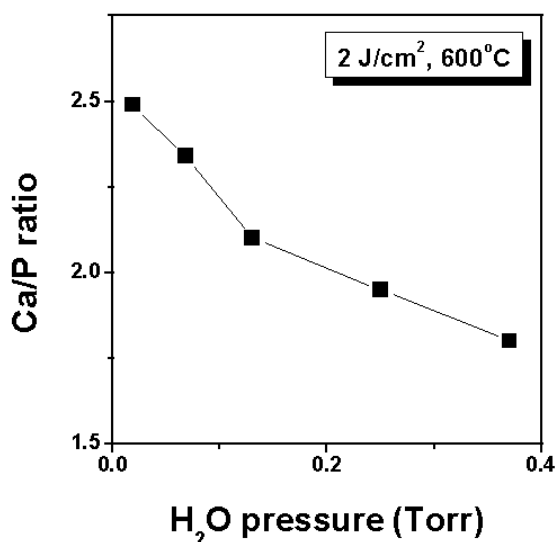
Fig. 5. Ca/P ratios of the films measured by energy dispersive X-ray spectroscopy (EDX). The films were deposited at 600 °C under various H_2O pressures with a laser fluence of 2 J/cm^2.

Fig. 6. X-ray diffraction patterns of the films deposited at 600 °C under various H_2O pressures with a laser fluence of 2 J/cm^2.

tion pattern exhibited the peaks from tetracalcium phosphate [TTCP, $Ca_4O(PO_4)_2$], CaO, and a small amount of HA. This coincides with the high Ca/P ratio in Fig. 5. The high Ca/P ratio of the film resulted in the formation of high Ca/P phases, such as CaO and TTCP (Ca/P = 2). As the H_2O pressure was increased, the peaks from TTCP and CaO gradually vanished, and the intensity of HA increased. Under H_2O pressures greater than 0.13 Torr, all peaks observed were from HA. H_2O promoted the formation of HA by not only decreasing the Ca/P ratio but also providing OH^- groups.

Since the total amount of deposited material was almost constant (Fig. 2) and the Ca/P ratio decreased with H_2O pressure (Fig. 5), the amount of phosphorus in the film should increase with increasing H_2O pressure whereas the amount of calcium should decrease. As mentioned afore, the decrease in calcium deposition can be explained by a scattering of the plume with the background gas. Regarding phosphorus, however, the phosphorus deposition increased with the H_2O pressure despite plume scattering. The preferential resputtering phenomenon is likely to be more important than plume scattering for determining the amount of deposited phosphorus. A preferential resputtering of phosphorus from a calcium phosphate film was observed during the sputter deposition of calcium phosphate films [24], and an increase in the background O_2 pressure resulted in a better stoichiometry (lower Ca/P ratio) of the film [25]. This is in good agreement with the relationship between the Ca/P ratio and the H_2O pressure obtained for the PLD process in this study.
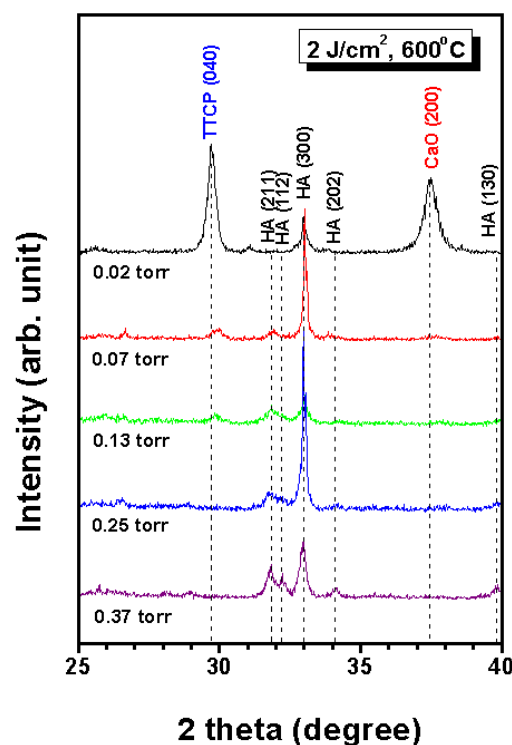
IV. CONCLUSION

Calcium phosphate films were prepared by using a PLD technique with pure HA targets under a wide range of H_2O pressures. With increasing H_2O pressure, the growth rate increased, and the mass deposited was almost constant. Consequently, the density gradually decreased with H_2O pressure, resulting in a porous microstructure under 0.37 Torr. The Ca/P ratio of the film decreased with H_2O pressure, and the crystal structure of the deposited film changed in accordance with the Ca/P ratio. The observed peaks were all from HA under H_2O pressures larger than 0.13 Torr, and the peaks from high Ca/P phases, such as TTCP and CaO, dominated for the film deposited at 0.02 Torr. A high-density HA film with a high degree of crystallinity could be obtained under a H_2O pressure of 0.25 Torr at a substrate temperature of 600 °C.

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