# Influences of Ambient Gases on the Structure and the Composition of Calcium Phosphate Films Prepared by Pulsed Laser Deposition

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Calcium phosphate films were prepared by using a pulsed KrF-laser deposition (PLD) method with a hydroxyapatite target in various ambient gases, such as Ar, $O_2$ and $H_2O$. The influence of the ambient gas on the properties of the deposited films was investigated. The chamber pressure and the substrate temperature were fixed at 0.25 Torr and 600 °C, respectively. Calcium-rich amorphous calcium phosphate films were deposited with a low density in Ar due to the preferential resputtering of phosphorus from the growing film. In an $O_2$ ambient, the density and the Ca/P ratio of the films were similar to those of the target. However, the deposited film was amorphous calcium phosphate and did not contain $OH^-$ groups. Polycrystalline hydroxyapatite films can be deposited in a $H_2O$ ambient because a sufficient supply of $OH^-$ groups from the ambient gas is essential for the growth of a hydroxyapatite film.

## I. INTRODUCTION

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, has been used as a biomedical material for many applications in both dentistry and orthopedics because it is the main chemical component of bone [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 [1]. The solution is to apply HA as a coating on titanium implants [3, 4]. In this way, the mechanical properties of the implants are supported by the substrate while the osteointegration is promoted by the bioactive surface of HA. Plasma-spray (PS) [5] was the first method used for coating implants with HA and the PS coatings exhibited faster bone healing than uncoated implants [2, 6]. The main problems of PS coatings are related with the low degree of HA's crystallinity and its porosity [6–8]. As a result, PS coatings exhibit fast dissolution in human plasma [9,10]. The dissolution rate in human plasma is one of the most important parameters in the long-term behavior of medical implants because the coating should be maintained on metallic substrate until complete bonding is formed between bone and implant.

Pulsed laser deposition (PLD) is one of the most flexible methods for depositing complex multielemental oxides [11,12] and PLD of HA thin films has been investigated as an alternative to PS [13–20]. Amorphous films have been deposited at substrate temperatures below 400 °C [11]. Also crystalline films have been reported to be produced at elevated temperatures [13–18]. Crystalline HA films were deposited without impurity phases on titanium substrates in $Ar/H_2O$ at 590 °C [17] and a-tricalcium phosphate or $\beta$-tricalcium phosphate films were deposited in $O_2$ [13]. The PLD HA films showed low dissolution rates in various simulated body fluids [19,20]. Many reports focused on the deposition of the HA phase in $H_2O$-containing ambient gases, but the influence of the ambient gases on the structure and the composition of the deposited film has not been studied comparatively.

In this study, the effects of ambient gases on the structure and the composition of PLD calcium phosphate films were addressed. The films were deposited on pure titanium substrates in various ambient gases, such as Ar, $O_2$ and $H_2O$. Then, the phase, chemical composition, density and surface morphology of the deposited films were characterized.
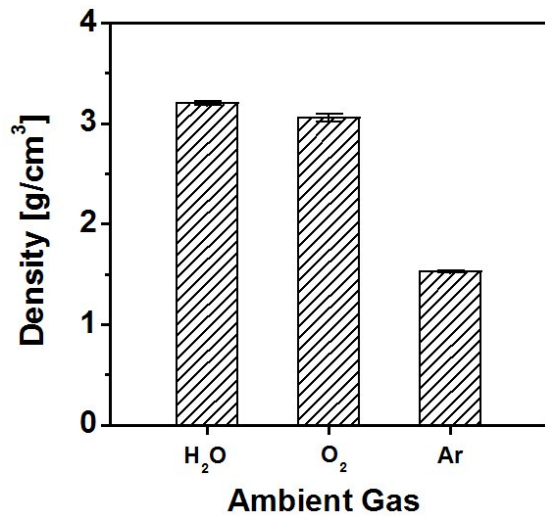
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Fig. 1. Densities of the films deposited in various ambient gases.



Fig. 2. Surface morphologies of the films deposited on Ti substrates in (a) $H_2O$, (b) $O_2$ and (c) Ar.

## II. EXPERIMENTS

Sintered HA discs were used as the target for PLD. The density of the target was 2.94 g/cm$^3$. The substrates were finely polished pure Ti discs (10 mm $\phi \times 1$ mm). The films were deposited in a vacuum chamber by utilizing a pulsed KrF laser (TuiLaser ThinFilmStar 20, 20 Hz, 2 J/cm$^2$) at a substrate temperature of 600 °C. Ar, $O_2$ and $H_2O$ were compared as the ambient gas for PLD and the pressure of ambient gas was maintained at 0.25 Torr during the deposition. The details of the PLD system and process are described elsewhere [18]. The thickness of the films was fixed at 1 $\mu$m by controlling the number of laser pulses.

In order to determine the deposition rate of PLD films, we measured the thickness of the deposited film by using a scanning electron microscope (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. Raman spectroscopy and X-ray diffraction (XRD) were 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. Raman spectroscopy was more useful than X-ray diffraction because it is able to detect amorphous phases, as well as crystalline phases. Fourier-transform infrared (FTIR) analysis was also performed to characterize the OH$^-$ group in the films. The surface morphology of the films was observed using a SEM and the root-mean-square (RMS) roughness was determined by using an atomic force microscope (AFM).
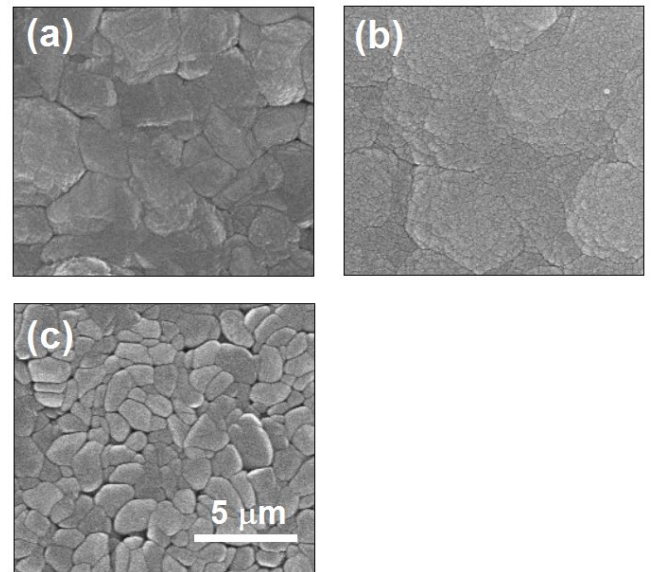
Table 1. RMS roughnesses of the Ti substrate and the deposited films.

| Material | | RMS roughness (nm) |
|---|---|---|
| Substrate | | 123 |
| Film | deposited in $H_2O$ | 166 |
| | deposited in $O_2$ | 177 |
| | deposited in Ar | 209 |

## III. RESULTS AND DISCUSSION

Since the Ti substrate is easily oxidized at elevated temperatures in oxidizing ambient gases, both the oxidation of the substrate and the deposition of film increase the mass of the sample. In order to eliminate the effect of oxidation of Ti, we measured the change in the mass during the deposition with and without exposure of the target to the laser beam. Then, the difference was calculated to determine the mass of the deposited film. Ti substrates were readily oxidized in $H_2O$ or $O_2$, resulting in an increase in the mass, whereas the mass of the Ti substrate did not change in Ar without a laser beam. Since the thickness of all films was fixed at 1 $\mu$m by controlling the number of laser pulses, the mass was proportional to the density of the deposited film. The results are shown in Fig. 1. The density of the film deposited in $H_2O$ was almost the same as that of bulk HA and the film deposited in $O_2$ showed a slightly lower density. However, the film deposited in Ar showed a low density that was approximately 50 % of that of the film deposited $H_2O$.

The surface morphology and the RMS roughness of the deposited films are shown in Fig. 2 and Table 1,
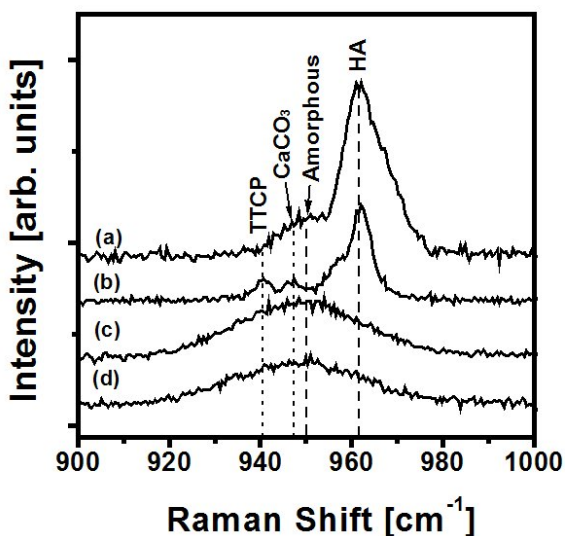
Fig. 3. Raman spectra obtained from (a) the target (sintered hydroxyapatite) and the films deposited on Ti substrates in (b) $H_2O$, (c) $O_2$ and (d) Ar.
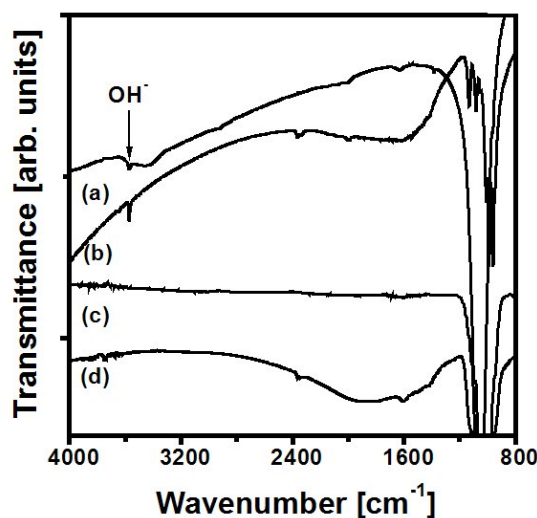


Fig. 4. FTIR spectra obtained from (a) the target (sintered hydroxyapatite) and the films deposited on Ti substrates in (b) $H_2O$, (c) $O_2$ and (d) Ar.

Table 2. Ca/P ratios of the hydroxyapatite targets and the deposited films.

| Material | | Ca/P Ratio |
|---|---|---|
| Target | before sintering | 1.71 |
| | after sintering | 1.84 |
| Film | deposited in $H_2O$ | 1.78 |
| | deposited in $O_2$ | 1.88 |
| | deposited in Ar | 2.15 |

respectively. The films deposited in $H_2O$ or $O_2$ showed relatively smooth surfaces whereas the films deposited in Ar exhibited rough surfaces with pores. These results agree well with the low density for the Ar case in Fig. 1.

The Raman spectra of the samples are shown in Fig. 3. The film deposited in $H_2O$ only exhibited peaks from crystalline phases [16,21], such as HA (962 $cm^{-1}$), tetra-calcium phosphate (TTCP, 941 $cm^{-1}$) and $CaCO_3$ (947 $cm^{-1}$). Considering the intensities of the peaks, the film deposited in $H_2O$ consists mainly of HA and contains small amounts of tetracalcium phosphate and $CaCO_3$. Contrarily, the Raman spectra from the films deposited in $O_2$ or Ar had only an amorphous peak at 950 $cm^{-1}$. We suspect that $H_2O$ promoted the formation of HA by providing $OH^-$ groups to the growing film because $H_2O$ was the only gas that could deposit crystalline HA on Ti substrate in our study.

FTIR analysis was performed to compare the amount of the $OH^-$ group in the target (sintered HA) and in the films deposited in $H_2O$ or in another gas, as shown in Fig. 4. The peak from $OH^-$ was found at 3570 $cm^{-1}$ [22,23] for the film deposited in $H_2O$, as well as the target. The films deposited in Ar and $O_2$, however, did not show the $OH^-$ peak. Hydroxyl groups released from the

target are easily pumped away, or hydroxyl groups at the substrate are preferentially sputtered out of the growing film. Thus, a sufficient supply of $OH^-$ groups from the ambient gas is essential for the growth of crystalline HA.

Table 2 shows the Ca/P ratios of the target and the films. The Ca/P ratio increased from 1.71 to 1.84 during sintering of target material and the films deposited in $H_2O$ and $O_2$ showed Ca/P ratios similar to that of the sintered target. Contrary to that, the film deposited in Ar showed a higher Ca/P ratio of 2.15.

In hydroxyapatite, phosphorus is bound as $PO_4$, so higher Ca/P ratio can be caused by preferential resputtering of phosphorus before $PO_4$ is formed in the growing film. In a previous work [18], we observed an increased amount of phosphorus in PLD films with increasing $H_2O$ pressure although the flux of phosphorus from the target should be reduced by scattering of the plume by the background gas. Therefore, the preferential resputtering of phosphorus from the growing film by the plume is important for determining the amount of deposited phosphorus. A preferential resputtering of phosphorus from a calcium phosphate film was also reported by van Dijk *et al.* [24,25] for the sputter deposition of the film from a HA target. They demonstrated that the Ca/P ratio increased to more than 12 with increasing external negative bias power on the substrate to 100 W, which means that resputtering of phosphorus by an energetic depositing flux is much faster than that of calcium. They also reported that a better stoichiometry of the deposited films with respect to HA was obtained by the introduction of $O_2$ into the sputter gas, which is in good accord with the experimental results in Table 2. In the PLD process of this work, an oxidizing ambient gas, such as $H_2O$ or $O_2$, reacts with the growing film to enhance the formation of $PO_4$ in the film. Consequently, preferential

resputtering of phosphorus is suppressed by an oxidizing ambient gas, resulting in Ca/P ratios that are lower than those obtained with an Ar ambient gas.

## IV. CONCLUSION

The influence of the ambient gas on the structure and the composition of calcium phosphate films was investigated. Polycrystalline HA films can be deposited in a $H_2O$ ambient because a sufficient supply of $OH^-$ groups is essential for the growth of HA. The density and the Ca/P ratio of the films deposited in $O_2$ were similar to those of the films deposited in $H_2O$; however, the deposited film was amorphous. In an Ar ambient, low-density calcium-rich amorphous calcium phosphate films were deposited due to the preferential resputtering of phosphorus from the growing film.

## ACKNOWLEDGMENTS

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