Journal of the Korean Physical Society, Vol. 49, No. 6, December 2006, pp. 2418∼2422

Influence of Substrate Temperature on the Growth Rate and the Composition of Calcium Phosphate Films Prepared by Using Pulsed Laser Deposition

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(Received 28 September 2006)

Calcium phosphate films were prepared by using a pulsed laser deposition (PLD) technique with a KrF excimer laser (248 nm, 2 J/cm^2), and the influence of the substrate temperature on the growth rate and the composition of those films was studied at substrate temperatures ranging from room temperature to 700 °C. Sintered hydroxyapatite (HA) was used as the target, and the films were deposited under 0.25 Torr of H_2O. The temperature dependency of the erosion of the film by the energetic deposition flux is also discussed. The substrate temperature critically affected the growth rate and the composition of the deposited films. The mass of the PLD calcium phosphate film decreased 8 % with increasing substrate temperature from room temperature to 700 °C, and this was explained by enhanced sublimation of the film by the bombardment of the deposition flux at higher substrate temperatures. The Ca/P ratio also gradually increased from 1.7 to 1.9 with increasing temperature because the amount of phosphorus sublimated from the growing film increased more rapidly as compared with the amount of calcium that sublimated. A high density and a strong (300) preferred orientation were also observed at high substrate temperatures.

PACS numbers: 81.15.Fg, 68.55.Jk, 68.55.Nq
Keywords: Pulsed laser deposition, Calcium phosphate, Hydroxyapatite, Substrate temperature

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 are some issues affecting the long-term stability and the coating-substrate adhesion of PS coated implants. The main problems are related with the properties of the coating layer: low density and the presence of amorphous and other crystalline calcium phosphate phases [6–8]. As an alternative method for HA deposition, pulsed laser deposition (PLD) has been investigated to produce thin HA films with high crystallinity and good adhesion. PLD is one of the most flexible methods for depositing complex multi-elemental oxides [9–12]. It was reported that crystalline HA thin films could be produced using ultraviolet lasers, such as KrF [13–15], ArF [15–18], or Nd:YAG [19,20].

Many research efforts have been reported on the influence of the process parameters on the crystal structure of the deposited film. There have been works studying the effect of substrate temperature on the crystal structure and on the chemical composition of the deposited film by using a KrF [13,14], ArF [18], or Nd:YAG [20] laser. Substrate temperatures over 400 °C are required to obtain crystalline films, and reactive ambient gases containing water vapor (H_2O) are essential for deposit-

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ing HA films. In H_2O-enriched Ar environments, deposition of hydroxyapatite was observed at temperatures between 400 and 700 °C, and tetracalcium phosphate [$Ca_4O(PO_4)_2$, tetraCP] was observed above 700 °C [13]. The Ca/P ratio of the deposited film increases with increasing deposition temperature [14,18,20]. However, the influence of the substrate temperature on the deposition kinetics has received little attention.

In previous works, we studied the effects of the environmental gas and the chamber pressure on the crystal structure of calcium phosphate films prepared by using pulsed KrF laser deposition [21,22]. A high-density HA film was obtained under a H_2O pressure of 0.25 Torr at a substrate temperature of 600 °C. In this work, the effect of substrate temperature was studied. Calcium phosphate films were deposited at substrate temperatures between room temperature and 700 °C, and the mass, thickness, crystal structure and composition of the deposited films were examined. The deposition kinetics is discussed in terms of sublimation and sputtering.

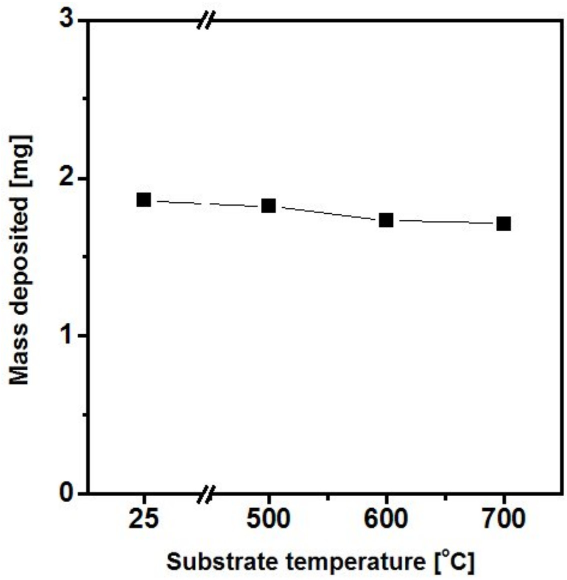

Fig. 1. Mass of the film as a function of the substrate temperature under 0.25 Torr of H_2O with a laser fluence of 2 J/cm^2. The number of shots was fixed at 2.8×10^4.

II. EXPERIMENTS

A Si wafer with a 100-nm-thick thermal oxide layer was used as the substrate. 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. Sintered HA discs were used as targets for PLD, and the laser beam was focused on the rotating target at an angle of 45 °C. The fluence of the KrF laser was 2 J/cm^2. The details of the PLD process are described elsewhere [21]. The films were deposited under 0.25 Torr of pure H_2O at various substrate temperatures ranging from room temperature to 700 °C.

In order to determine the deposition rate of PLD films, we used a scanning electron microscope (SEM) to measure the thickness of the deposited film. 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. The surface morphology of the film was observed using a SEM. X-ray diffraction (XRD) was used to investigate the crystal structures and the preferred orientations of the films, and energy dispersive X-ray spectroscopy (EDX) was used to measure the atomic concentrations of the elements, such as Ca, P and O, composing the film.

III. RESULTS AND DISCUSSION

Fig. 1 shows the mass of the deposited film as a function of the substrate temperature under 0.25 Torr of H_2O. The fluence and the number of shots of the laser pulse were fixed at 2 J/cm^2 and 2.8×10^4, respectively. The mass of the film decreased 8 % with increasing substrate temperature from room temperature to 700 °C. This decrease in the deposited mass was related with increased erosion of the growing film by energetic particle bombardment at elevated temperatures. In the PLD process, the deposition flux from the target, the "plume", is so energetic that the particles have kinetic energies comparable to the bond strength in the growing film. High-energy tails with energies above 50 eV can cause material to be re-sputtered from the film surface [10] even at room temperature; however, the physical sputtering itself is independent of the substrate temperature. In considering the melting temperature of HA (T_m, 1670 °C), the sublimation should be very slow even at 700 °C (∼1/2 of T_m). The relatively high values and the temperature dependency of the erosion rate can be explained as the creation of surface adatoms by the particle bombardment and their subsequent sublimation at high temperatures [23]. It can be easily found in the literature that the experimentally measured erosion rate of solid surfaces by energetic particle bombardment at elevated temperatures exceeds that predicted by a summation of the physical sputtering rate and the sublimation rate [24–26]. In order to investigate the effect of substrate temperature on the amounts of materials removed from the film, we placed a Si wafer beside the target during deposition; then, we analyzed its chemical composition by using EDX. The results are shown in Fig. 2. Higher concentrations of Ca and P were obtained for the deposition at 700 °C than for the deposition at room temperature. This is evidence for more erosion of the

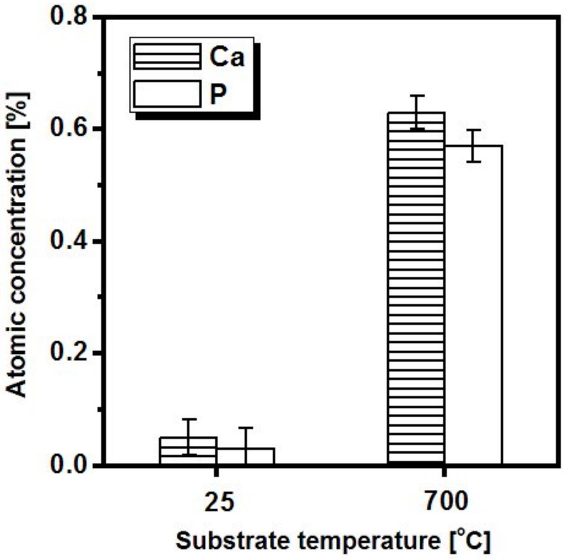

Fig. 2. Atomic concentration of Ca and P measured by EDX from a wafer placed besides the target during PLD. The number of shots was 2.8×10^4. A thin calcium phosphate layer was formed on the wafer due to the sublimation of the growing film.

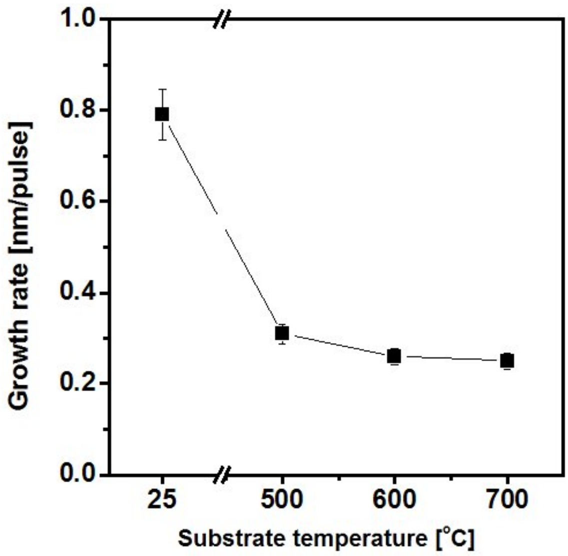

Fig. 3. Growth rate of the film as a function of the substrate temperature under 0.25 Torr of H_2O with a laser fluence of 2 J/cm^2.

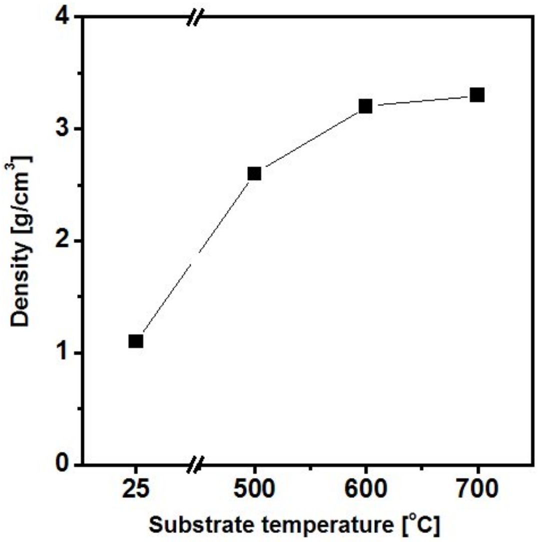

Fig. 4. Density of the film as a function of the substrate temperature under 0.25 Torr of H_2O with a laser fluence of 2 J/cm^2.

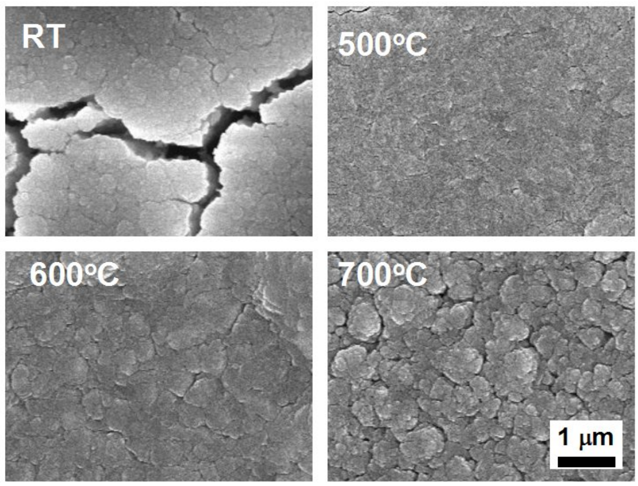

Fig. 5. Surface morphologies of the films deposited at various substrate temperatures under 0.25 Torr of H_2O with a laser fluence of 2 J/cm^2. The thickness of the film was fixed at 7 μm.

film at higher substrate temperatures.

Fig. 3 shows that growth rate of the film as a function of the substrate temperature. The growth rate rapidly decreased as the temperature increased from room temperature and 500 °C, and then slightly decreased with increasing substrate temperature from 500 to 700 °C. Since the change in the mass (Fig. 1) is relatively smaller than the change in the deposition rate (Fig. 3), the change in the deposition rate is mainly due to the change in the film density with increasing substrate temperature. The densities of the films were calculated from the masses and the volumes of the deposited films and are shown in Fig. 4. The density of the film increased with increasing substrate temperature and was almost the same as that of bulk HA (3.15 g/cm^3) at substrate temperatures of 600 and 700 °C, whereas the density was approximately 35 % that of the bulk HA at room temperature. Since surface diffusion on the growing film is promoted by the elevated substrate temperature, high-density films were obtained at high substrate temperatures.

Fig. 5 shows the surface morphologies of the films deposited at various substrate temperatures. The thickness

Table 1. Ca/P ratios of the hydroxyapatite targets and the deposited films.

Substrate temperature	Room temperature	500 °C	600 °C	700 °C
Ca/P ratio	1.67	1.71	1.73	1.91

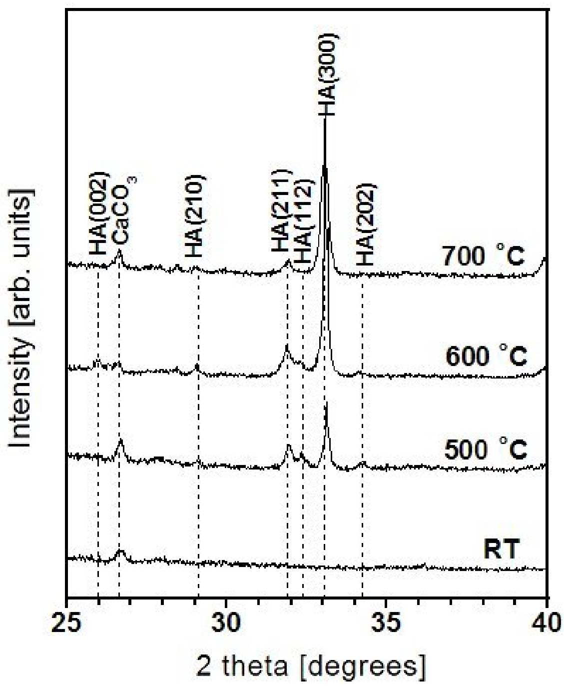

Fig. 6. X-ray diffraction patterns of the target and the films deposited at various substrate temperatures under 0.25 Torr of H_2O with a laser fluence of 2 J/cm^2.

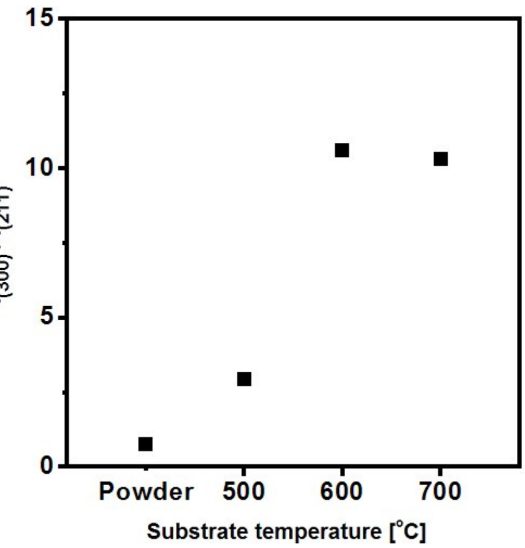

Fig. 7. Intensity ratios of (300) to (211) calculated from the powder and the films deposited at various substrate temperatures under 0.25 Torr of H_2O with a laser fluence of 2 J/cm^2.

of the films was fixed at 7 μm by controlling the number of laser pulses. When the substrate was not heated, the deposited film contained many cracks on the surface. The film deposited at room temperature was mechanically very weak and did not adhere well to the substrate, resulting in a failure in the Scotch tape test. However, neither pores nor cracks were observed for the films deposited at elevated temperatures, and all films adhered well to the substrates. The surfaces of the films looked relatively smooth compared with those for another group [20], and the grain structure started to evolve with increasing substrate temperature.

The chemical composition and the constituent phases of the films were analyzed using the EDX and the XRD techniques. The Ca/P ratio determined using EDX gradually increased from 1.7 to 1.9 with increasing substrate temperature, as shown in Table 1. This result agrees well with other groups' reports [14,18,20]. The increase in the Ca/P ratio with increasing temperature can also be explained by an increase in the erosion of the growing film by the plume. In Fig. 2, the amounts of materials ejected from the growing film increased with temperature, and the Ca/P ratio was approximately 1.2 regardless of the substrate temperature, which is significantly lower than that of HA (1.67). Therefore, the amount of phosphorus removed from the growing film increased with temperature more rapidly than that of calcium did, resulting in a higher Ca/P ratio at higher substrate temperatures.

Fig. 6 shows the XRD patterns obtained from the deposited films. No peaks from HA were observed from the film deposited at room temperature while HA peaks were observed from the films deposited at elevated temperatures. However, the relative intensities of the HA peaks varied greatly with temperature; the intensities of the (211) and the (112) peaks gradually decreased whereas the intensity of the (300) peak reached its maximum at 600 °C. Since the largest peak for the powder diffraction pattern [27] is the (211) peak, we calculated the intensity ratio of the (300) to the (211) peak from Fig. 6, and the results are shown in Fig. 7. The intensity ratio of the (300) to the (211) peak was 0.75 for powders. Contrary to that, the ratios were more than 10 for the films deposited at 600 or 700 °C, suggesting strong a (300) preferred orientation of the PLD HA films.

IV. CONCLUSION

The substrate temperature critically affected the growth rate and the composition of the deposited films.

The mass of the PLD calcium phosphate film decreased 8 % with increasing substrate temperature from room temperature to 700 °C. More erosion of the film by energetic particle ("plume") bombardment was observed at higher substrate temperatures and was explained as the creation of surface adatoms by particle bombardment and their subsequent sublimation at higher temperatures. The Ca/P ratio also gradually increased from 1.7 to 1.9 with increasing temperature because the amount of phosphorus sublimating from the growing film increased more rapidly as compared with the amount of calcium the sublimated. The density of the film increased with increasing substrate temperature, and the (300) preferred orientation became stronger.

ACKNOWLEDGMENTS

This work was supported by grant No. R01-2003-000-10565-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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