Effect of Laser Fluence on Poly-crystallization of Hydroxyapatite Film Coated by PLD Method

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We successfully obtaineed the poly-crystallized coatings of the bioactive hydroxyapatite (HAp) on the titanium plates at room temperature. We used several ceramics HAp targets prepared by sintering at different temperature of 500°C, 700°C, 900°C and 1100°C. These targets were ablated by the KrF excimer laser with fluence of 4J/cm^2, 5J/cm^2 and 6J/cm^2. The film depositions were performed under 1 Torr H_2O atmosphere. The amount of HAp polycrystals increased as the laser fluence rised. The film deposited from a target sintered at 900°C included a much amount of the crystalline of HAp. We concluded that the ablated species had different energies depending on both the target density and the laser fluence. It resulted in the difference of migration and crystallization of the HAp film.

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1. Introduction

Hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is bioactive and biocompatible material and has been studied widely for a coating material. HAp coating was one of the candidates for improving the durability and biocompatibility of implants and artificial bones. Among the various HAp coating methods, the pulsed laser deposition (PLD) method was first introduced in 1992 [1]. Some researchers used excimer lasers for the ablation [1-5] and the others used the harmonics of Nd:YAG lasers [6,7]. In the previous studies, the substrates of Ti and/or Ti-alloy were maintained at high temperatures between 500ºC and 800ºC in the water vapor atmosphere in order to obtain a high degree of crystallinity [1-7]. It was pointed out that this condition promoted the oxidation of the substrate surface prior to the growth of the HAp layer and then degraded the adhesion of the coating to the substrate [8,9]. Therefore, the crystallized HAp coatings should be fabricated at lower temperatures to avoid extensive oxidation of the substrate. Craciun *et al.* proposed the vacuum ultraviolet (VUV) annealing to improve the crystallinity of HAp coatings [10]. They used the Xe_2* excimer lamp with the purpose of a photo-chemical annealing. We also have developed a new HAp coating method using two UV excimer laser beams. This method, which we called laser assisted laser ablation (LALA) method, was based on PLD and employed the second laser as an 'assist laser' to anneal the film and the substrate. We have found that irradiation of the assist laser beam improved not only the adhesion but also crystallinity of the coatings [11-13]. When we stopped irradiating the assist laser, the films contained the amorphous phase. If we can obtain a poly-crystallized HAp by a simple PLD scheme under the room temperature without heating the substrate and post-annealing, it was possible to improve the crystallinity of the coating furthermore using a LALA method.

We have been trying to deposit the poly-crystal HAp by a PLD method using HAp ceramics targets sintered at various temperatures. The density of HAp target was varied according to the sintering temperature. We successfully obtained a poly-crystallized HAp films on the Ti substrate at room temperature using a HAp ceramics targets sintered at temperatures of 900ºC [14]. We measured the currents from the ablated ions from the HAp ceramics targets and investigated the relationship between the relationship between the crystallinity of the coatings and the energy distribution of the charged fragments from the HAp ceramics targets. We found that the ablated ions from the HAp ceramics targets with different densities had different energy distributions [15].

In this paper, we investigated the effect of the laser fluence to the crystallinity of HAp coatings. We prospected that higher laser fluence induced the higher energy of the ablated particles and much crystalline phase should be obtained in the deposited layer.

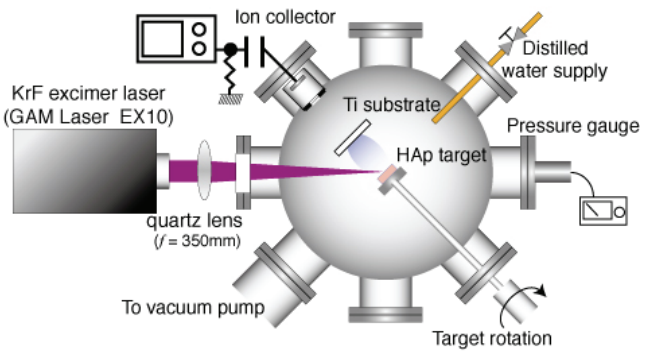

Fig. 1 PLD apparatus for HAp coating.

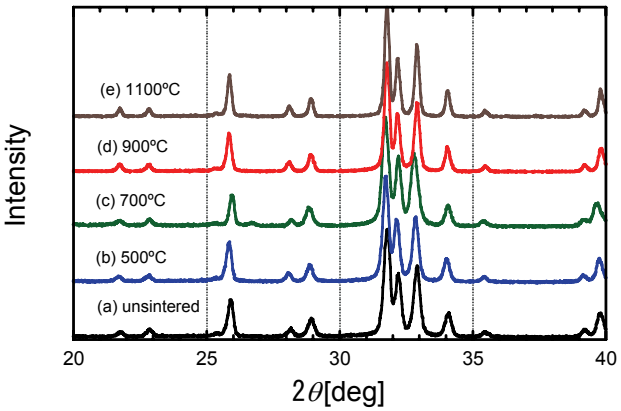

Fig. 2 XRD patterns of HAp ceramics targets (a) before and (b)-(e)after sintering.

2. Experimentals

The deposition was performed by an ordinary PLD scheme using a KrF excimer laser (GAM Laser, EX-10, λ=248nm, pulse width =15ns), as shown in Fig.1. The KrF excimer laser beam was focused by a quartz lens (*f*=350mm) and was irradiated on the target surface at a repetition rate of 100Hz and at an angle of incidence of 45º. The laser fluence was varied at 4J/cm^2, 5J/cm^2 and 6J/cm^2 by changing the discharge voltage of the laser. The ablated particles from the target were deposited on the polished Ti substrates, which were positioned on the stage normal to the target at a distance of 20mm.

HAp targets were made of HAp powder, HAP-200 distributed from Taihei Chemical Industry Co., Ltd. We compressed the powder by a pressure of 150MPa to make pellets. Then the HAp ceramics targets were fabricated by sintering the pellets for 10hr. in air at temperatures of 500ºC, 700ºC, 900ºC and 1100ºC using an electrical oven. The sintering temperature varied the densities of the HAp targets in the range from 1.5 to 2.4mg/mm^3, which were in proportional to the sintering temperature.

The target was rotated during the whole deposition period of 10min. The deposition chamber had a base pressure of 10^{-3}Torr and then the distilled water was supplied from a water tank into the chamber. The water vapor pressure was kept at an equilibrium pressure of 1.0Torr by adjusting the precision flow valve. After the deposition, the films were characterized by scanning electron microscope (SEM) and X-ray diffractometry (XRD).

3. Results and Discussion

In Fig. 2, the XRD patterns of the HAp ceramics targets, sintered at each temperatures. We found no other peak except for indicating the HAp. Then, we can concluded that all the targets contained the HAp poly-crystallines and decomposition was not observed even after sintering at the temperature of 1100ºC.

SEM images of the film surface deposited by the laser ablation were shown in Fig.3. All surfaces were filled with particles with a diameter of 5μm and also included large debris. The amount of debris decreased as the sintering temperature of the targets rising. The film thickness was also estimated and had a constant value of about 15μm.

In Fig. 4, the XRD patterns of the coatings deposited by 4J/cm^2 laser ablation were shown. In all XRD results, peak intensity were normalized at the peak intensity of titanium at 2θ=38.8º. In Fig. 4, several HAp peaks, for exam-

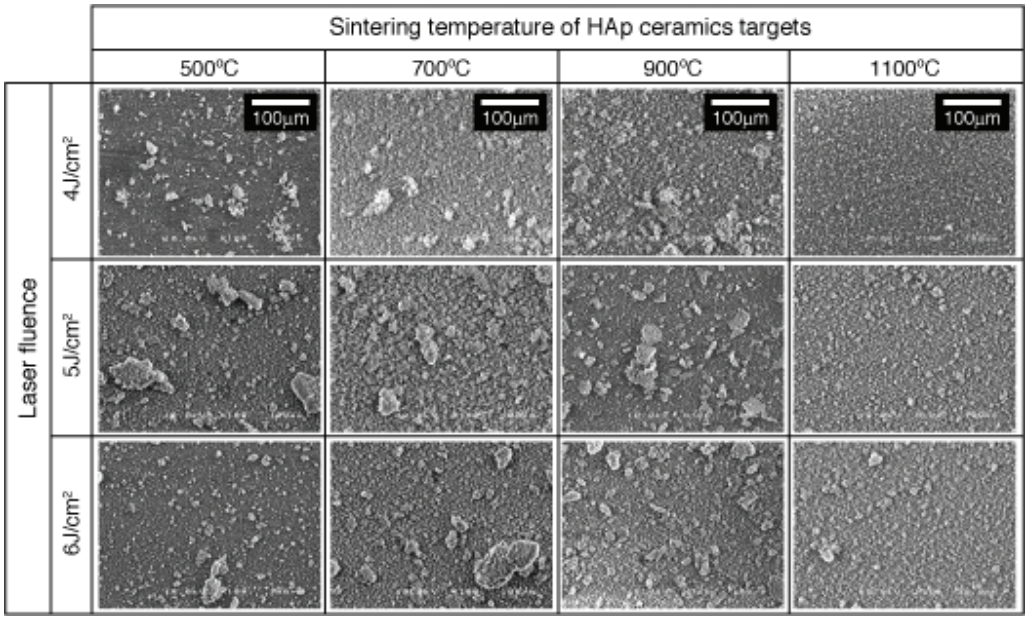

Fig. 3 SEM images of HAp films deposited by PLD methods.

ple, at 2θ=31.8º, 32.2º and 32.9º, were indicating that the poly-crystalline phase of HAp were obtained using the ceramics targets sintered at (a)500ºC, (b)700ºC and (c) 900ºC. A broadband signal around 2θ=25˚~35˚ indicated that the coatings contained some types of amorphous calcium phosphor species such as HAp, TTCP and $CaPO_4$.

In Fig. 5, the XRD patterns of the coatings deposited by 5J/cm^2 laser ablation were shown. The films deposited with targets sintered at (a)500ºC, (b)700ºC and (c)900ºC had significant peak of crystalline HAp phase. The height of the peaks gained compared to those of Fig. 4.

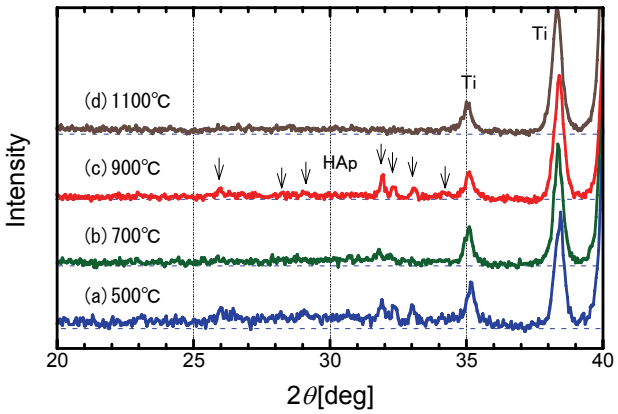

Fig. 4 XRD patterns of films deposited by laser fluence of 4J/cm^2.

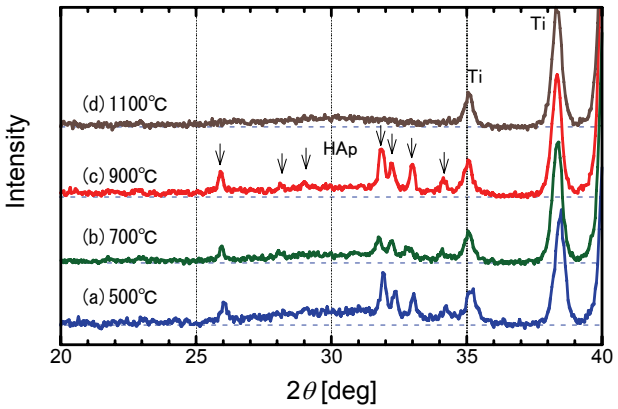

Fig. 5 XRD patterns of films deposited by laser fluence of 5J/cm^2.

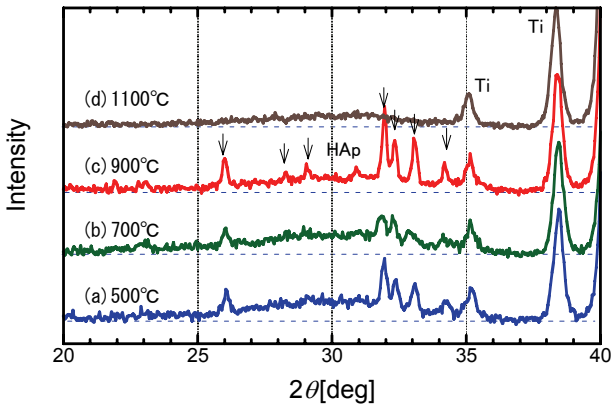

Fig. 6 XRD pattersn of films deposited by laser fluence of 6J/cm^2.

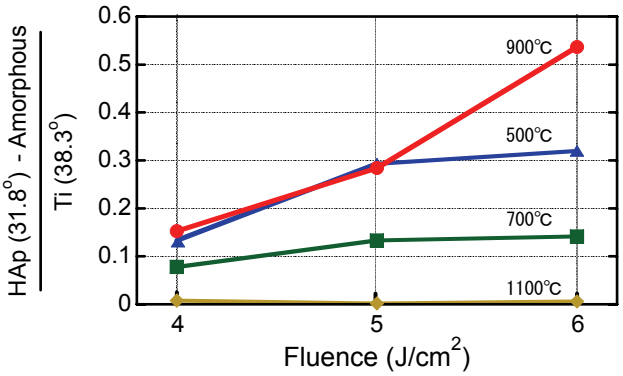

Fig. 7 XRD peak intensities plotted as a function of laser fluences.

The XRD patterns of the coatings deposited by 6J/cm^2 laser ablation were shown in Fig. 6. The films deposited with targets sintered at (a)500ºC, (b)700ºC and (c)900ºC had more significant peak of crystalline HAp phase. We can find that the laser fluence of the ablation laser went up from 4J/cm^2 to 6J/cm^2, and the peak intensity indicating the poly-crystalline phase had sufficiently increased.

From the results of XRD measurements, the peak intensities of the HAp poly-crystalline phase were estimated and plotted as a function the laser fluence, which was shown in Fig. 7. In Fig. 7, the ratio of the peak intensity of HAp at 2θ=31.8º to the peak intensity of Ti at 2θ=38.8º was calculated from the results of XRD measurements. When we estimated the peak intensity of crystalline HAp, we subtracted the broad band signals contributed by the amorphous calcium phosphor species from the intensity. We found that the amount of HAp poly-crystals in the deposited film was increasing in proportional to the ablation laser fluences. The amount of HAp poly-crystals in the film deposited with the target sintered at 900ºC was equal or larger than that with 500 ºC, taking account of the estimation error coming from the noise in the XRD data, and also significantly larger than those with the targets sintered at 700 ºC and 1100ºC,

In our previous result, as shown in Fig. 8[15], the total amounts and the kinetic energy distributions of the positive

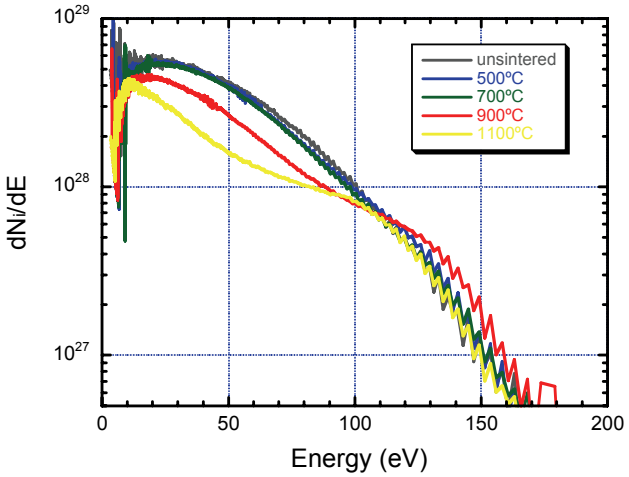

Fig. 8 Energy distributions of ablated ions from HAp ceramics targets sintered at different temperature.

ion from the targets sintered at 500ºC and 700ºC were almost same as that from the unsintered HAp pellet target. The total amount of positive ions was decreasing as the sintering temperature increased above 900ºC. The most amounts of positive ions having energies above 100eV were supplied from the target sintered at 900ºC. It concluded that the kinetic energy of the ablated fragments were important factor in order to deposit the crystallized coating and the target sintered at the temperature of 900ºC was the best to obtain the poly-crystalline film at room temperature. In this study, using a target sintered at 1100ºC, only the amorphous phase was contained in the deposited films. The energy distributions of ions, shown in Fig.8, represented that the amount of the ions from the 1100ºC sintering target was minimum in the energy range from 10eV to 100eV. The thickness of each film was almost same, about 15μm. From these results, we supposed that total amount of the fragments from each targets were almost same. The fragments supplied from the target sintered at 1100 ºC contained much amount of neutral species. On the other hands, the fragments supplied from the target sintered at 900ºC contained many ions with high energy. We concluded that the both mixture and energies of the ablated fragments were also important for the crystallization.

According to this point of view, when we increased the laser fluence in the rage from 4J/cm^2 to 6J/cm^2, the particles should gain the kinetic energy and the fragments contained many ions. It accelerated the migration of the particles at the surface and then poly-crystallization of the deposited HAp film would be promoted. In this study, we found the amount of the HAp poly-crystals had maximum value when we used a target sintered at 900ºC. We concluded that the best ceramics target was obtained after sintering at 900ºC.

4. Conclusion

We successfully deposited poly-crystallized hydroxyapatite(HAp) film at the room temperature. The crystallization of the HAp films were closely related to not only the sintering temperature of the targets but also the laser fluence. From the previous result of ion current measurement, the crystallization were affected by the energy of the ablated fragments and the ratio of fragments mixtures. High energy particles which were obtained by the high fluence laser ablation migrated and poly-crystallization was accelerated.

Acknowledgments

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