Crystallized hydroxyapatite coatings deposited by PLD with targets of different densities

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Crystallized hydroxyapatite coatings deposited by PLD with targets of different densities

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Abstract. We successfully achieved the poly-crystallized coatings of bio-active hydroxyapatite on titanium plates. We used several ceramic HAp targets sintered at a temperature of 500°C, 700°C, 900°C and 1100°C, and irradiation by KrF excimer laser at a fluence of about 4J/cm^2. The depositions were performed under 1Torr H_2O atmosphere at room temperature. In this condition, a poly-crystallized HAp layer was formed only using a target sintered at 900°C. We estimated the charged fragments from these targets by a simple ion-probe collection and found that the energy distribution of charged fragments depended on the densities of the targets.

1. Introduction

Hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$, HAp) has good biocompatibility and is being widely used as a coating material to improve the durability and biocompatibility of implant and alternative bone. Among the various HAp coating methods, the pulsed laser deposition (PLD) method was introduced in 1992 for high quality HAp coating [1] using excimer lasers [1-5] and some harmonics of Nd:YAG lasers [6,7]. In the previous studies, the substrates of Ti and/or Ti-alloy were maintained at temperatures between 500 and 800ºC in water vapor atmosphere in order to generate a HAp coating with a high degree of crystallinity for high biocompatibility [1-7]. The condition of high substrate temperature promoted the oxidation of the substrate surface prior to the growth of the HAp layer. The oxidation layer degraded the adhesion of the coating to the substrate [8, 9]. Therefore, crystallized HAp coatings should be deposited at lower temperatures in order to obtain a high adhesive coating.

Craciun et al. [10] showed that the post annealing method with the vacuum ultraviolet (VUV) improved the crystallinity of HAp coatings. They used an Xe_2^* excimer lamp as an annealing radiation source. We have developed a new HAp coating method using two UV excimer laser beams. This method, laser assisted laser ablation (LALA) method, is based on PLD and uses the second laser as an 'assist laser' to anneal the substrate. We found that irradiation with the assisted beam improved the adhesion and crystallinity of the coatings [11-13]. However, the HAp coatings were amorphous without these annealing laser irradiations. If a poly-crystallized layer is obtained by the simple PLD scheme without annealing process, it should be possible to improve the crystallinity of the coating.

We successfully deposited a poly-crystallized HAp film on the Ti substrate by PLD at room temperature with the HAp ceramic target sintered at temperatures of 900ºC [14]. The HAp targets

sintered at different temperature had different density. From the results, we presumed that the ablated fragments from the HAp ceramics with different densities had different energy distributions.

In this paper, we investigated the relationship between the characteristics between the crystallinity of the coatings and the energy distribution of the charged fragments from the HAp ceramics targets having various densities.

2. Experiments

HAp targets were made of HAp powder, HAP-200 distributed from Taihei Chemical Industry Co., Ltd. The HAp powder was compressed with a pressure of 150MPa to make HAp pellets. Then the ceramic targets were fabricated by sintering the pellets for 10hr in air at a temperature of 500ºC, 700ºC, 900ºC and 1100ºC using an electrical oven. The HAp targets had densities in the range from 1.5 to 2.4mg/mm^3, proportional to the sintering temperature. The crystallinity and the composition of these targets were confirmed to be kept after the sintering even at 1100ºC. The deposition was performed using an ordinary PLD scheme using a KrF excimer laser (GAM Laser, EX-10). The laser beam for the ablation was focused by a quartz lens (f=350mm) and was irradiated on the target surface with a fluence of approximately 4J/cm^2 and repetition rate of 100Hz at 45º angle of incidence. The ablated particles from the target were deposited on the polished Ti substrate, which was positioned on the stage normal to the target at a distance of 20mm. The target was rotated during the deposition period of 10min. The deposition chamber had a base pressure of 10^{-3}Torr. Distilled water was supplied into the chamber and the water vapor pressure was kept at an equilibrium pressure of 1.0Torr. The coating layer was characterized by scanning electron microscope (SEM) and X-ray diffractometry (XRD).

We estimated the energy of the charged fragments ablated from the HAp ceramic targets by means of a charge collector consisting of a copper electrostatic probe in the shape of a Faraday cup. The measurements were performed under the higher vacuum condition at a pressure of 2X10^{-5} Torr. The collector was placed at a distance of 80mm from the target. The KrF excimer laser was irradiated on the HAp ceramic targets with a fluence of 6J/cm^2 at 45º angle of incidence. We used the ceramic targets sintered at 500ºC, 700ºC, 900ºC and 1100ºC and also an unsintered HAp pellet. The positive ion currents caused by the ablated fragments were measured with the charge collector. Then, we assumed that all fragments were positive ions and the energies of the particles were calculated from the measured ion currents.

3. Results and Discussion

In Figures 1(a)-(d), SEM images of the deposited film surface are shown, with targets sintered at temperature of (a)500ºC, (b)700ºC, (c)900ºC and (d)1100ºC, respectively. Each film had a surface morphology of spherical particles with diameter of 5μm and some ablated debris. In figure 1, the film deposited from the target sintered at 900ºC contains smaller grains than those present in the films deposited from targets sintered at 500ºC, 700ºC and 1100ºC.

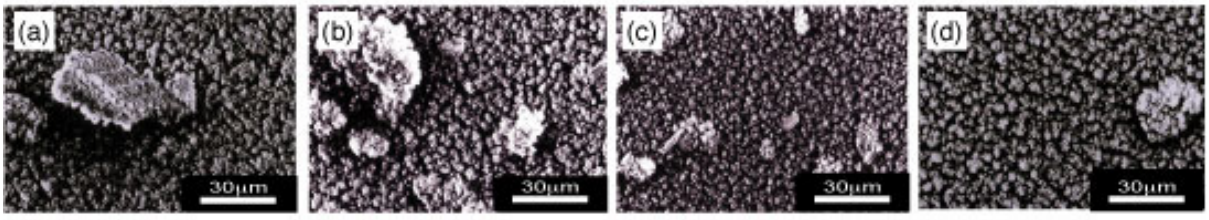

Figure 1. SEM images of coating surface deposited by PLD with HAp targets sintered at temperature of (a) 500ºC , (b) 700ºC, (c) 900ºC and (d) 1100ºC.

The XRD patterns of the deposited coatings are shown in figure 2(a)-(d). In Figure 2, the XRD patterns have broad peaks around 30˚. It means that all the coatings contain some type of amorphous calcium phosphor species such as HAp, TTCP and $CaPO_4$. In figure 2(a), (b) and (d), these films deposited with HAp ceramics sintered at (a)500ºC, (b)700ºC and (d)1100ºC have no significant peak of crystalline HAp phase. Only in a film deposited with a target sintered at 900ºC, shown in figure 2(c), the crystalline HAp peaks at around 26ºand 32º are obviously found. It concludes that only the film deposited with a HAp ceramic target sintered at 900ºC contains poly-crystallized HAp.

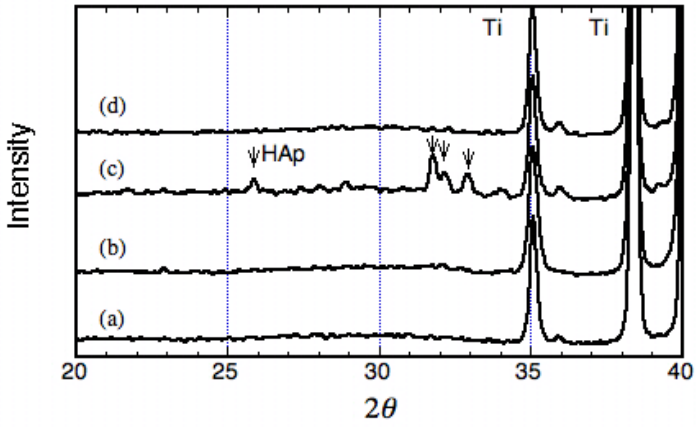

Figure 2. XRD patterns of coatings deposited with HAp targets sintered at temperature of (a) 500ºC, (b) 700ºC, (c) 900ºC and (d) 1100ºC.

In Figure 3, the energy distributions of the ablated fragments from the HAp ceramics targets are shown. The total amount of the positive ions from the targets sintered at 500ºC and 700ºC are almost same as that from the unsintered target. The amount of positive ions is decreasing as the sintering temperature increased above 900ºC. In the energy range above 100eV, the maximum number of the particles was obtained using the target sintered at 900ºC. It concludes that the positive ions with the energy above 100eV are important to fabricate the poly-crystallized HAp coating.

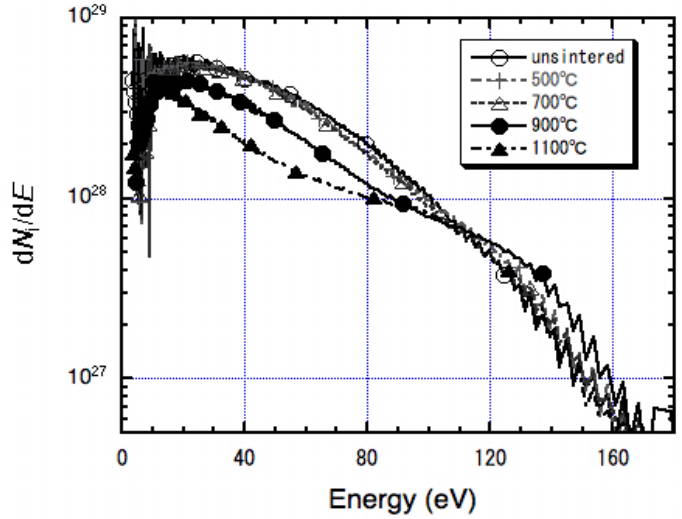

Figure 3. Energy distribution of charged fragments ablated from unsintered HAp pellet and HAp ceramics targets.

The measurements of the ion energies were performed under the vacuum condition at a pressure of $2X10^{-5}$Torr. On the other hands, the HAp films were deposited in the water vapor atmosphere of 1.0Torr. The fragments ablated from the HAp ceramics targets collides and reacts with the water vapor and then the energies of the particles decrease. When the particles come at the substrate, they grow up to film after the migration process on the substrate. Particles from the HAp ceramic target sintered at 900ºC, that have energy above 100eV, have sufficient energy for migration even after the collision with water molecules. Then, the coating included poly-crystalline phase. On the other hand, the low energy particles from the targets sintered at 500ºC, 700ºC and 1100ºC are in short supply of the migration energy. Then the coatings are amorphous. The energy of the ablated particle is important for migration on the deposited substrate. If we use the higher laser fluence and the lower water vapor

pressure, it is supposed that the particle energy go increase even with the targets sintered at 500ºC, 700ºC and 1100ºC and then the crystalline coatings should be obtained at room temperature.

4. Summary

Poly-crystallized HAp films were successfully deposited at room temperature by the PLD method. We successfully obtained a poly-crystalline HAp coating with a target sintered at 900ºC. We found a large amount of positive ions with energy above the 100eV were included in the ablated fragments. These fragments lost their energy due to the collision to the water vapor and then deposited on the Ti substrate. The energy of the ablated particle is important for migration on the deposited substrate.

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