

Fabrication of a *c*-axis tilted hydroxyapatite film using RF magnetron sputtering

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Abstract—In long bones, *c*-axes of Hydroxyapatite (HAp) crystallites are mainly oriented along the bone axis. The HAp coating film with same orientation may accelerate the bonding of the implant to the bone. In this study, fabrication of a *c*-axis tilted HAp film was performed using a RF magnetron sputtering system. The fabricated film sample was evaluated by the X-ray diffraction (XRD) and Transmission Electron Microscope (TEM) analyses.

I. INTRODUCTION

HAp is one of the main components of bones and teeth. HAp crystallites in bone are mostly hexagonal [1]. In bone, *c*-axes of HAp crystallites are mainly oriented along the bone axis direction [2]. It is known that the orientation of HAp on the implant surface in vivo gradually changes to the bone axis direction due to the stress [3]. Therefore, the surface coating of the implant by the oriented HAp film may improve the bonding speed to the bone. We then attempted to fabricate a HAp film and control the crystallites orientation via RF magnetron sputtering without epitaxial techniques. We first succeeded in fabricating a (001) oriented HAp film [4]. In this study, we attempted to fabricate a *c*-axis tilted HAp film.

II. EXPERIMENTS

The sputtering conditions are shown in Table 1. The crystallites orientation in the HAp film was evaluated by the 2θ - ω analysis of X-ray diffraction technique (X'Pert Pro MRD, PANalytical). The final film thickness (3-4 μm) was measured by using a contact-type thickness meter (SJ-400, Mitutoyo). We observed the crystalline phase and nanostructure of the film using Transmission Electron Microscope (TEM, JEOL JEM 2100F). Energy dispersive X-ray spectroscopy (EDX) and Selected area electron diffraction (SAED) measurements were also performed.

III. RESULTS AND DISCUSSION

Fig. 1 shows XRD 2θ - ω patterns of the sample at positions of 10-40 mm from the anode center. The HAp (112) peaks were found at $2\theta = 32.2^\circ$ at the positions of 30 mm and 40 mm. The TEM images of the film in the area showed that the tilt angles of the HAp crystallites from the normal direction were 25 degrees (30 mm) and 18 degrees (40 mm). EDX data showed that the Ca/P ratios in the film were 1.51 (30 mm) and 1.50 (40 mm), which were lower than the theoretical value of

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HAp (1.67). Therefore, a calcium-deficient HAp (CDHA, $\text{Ca}_{10-z}(\text{HPO}_4)_z(\text{PO}_4)_{6-z}(\text{OH})_{2-z}$, $Z = 0-1$, $\text{Ca/P} = 1.50-1.67$) film [5] was formed on the substrate surface. The calcium-deficient HAp is known as a substance that plays important roles in processes such as bone remodeling and bone formation [6]. From the results of SAED, the hexagonal phase was not observed at 30 mm, however, it was observed at 40 mm. At both positions, monoclinic phase was also observed. The film seems to have non-uniform mixed structure depending on the area.

TABLE I. Sputtering conditions

Atmospheric Gas	Ar : O ₂ =1:3, Total 0.1 Pa
Substrate	Silica glass plate
RF power	100 W
Deposition time	48 hour

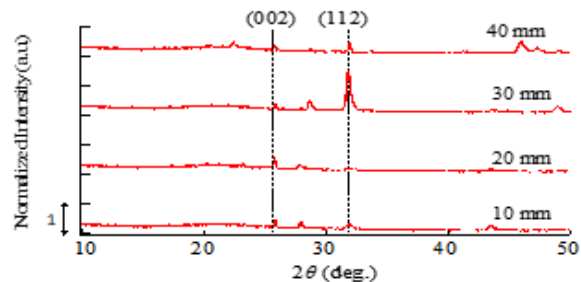


Figure 1. XRD 2θ - ω scanning patterns.

IV. CONCLUSION

The fabrication of a *c*-axis tilted Ca-def HAp film was performed on the glass substrate using a RF magnetron sputtering technique. However, the film seems non-uniform and the tilt angles of the *c*-axis of HAp crystallites were small. Our final goal is the control of the tilt angle and fabrication of an uniaxially aligned HAp crystallites film in plane. Further experimental studies are expected for better HAp films.

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REFERENCES

- [1] M. Aizawa, et al, Biol. Pharm. Bull. 36, 1654 (2013).
- [2] N. Sasaki, et al., Calcif Tissue Int, 60, 361 (1997).
- [3] T. Nakano, et al, ISIJ International, 51, 262 (2011).
- [4] K. Hirata, et al, AIP Advances, 7, 085219, (2017).
- [5] S. V. Dorozhkin, Materials, 2, 1975 (2009).
- [6] A. S. Posner, Physiol. Rev., 49, 760 (1969).