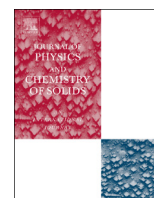




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## Control of composition and crystallinity in hydroxyapatite films deposited by electron cyclotron resonance plasma sputtering

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## ABSTRACT

Hydroxyapatite (HAp) films were deposited by electron cyclotron resonance plasma sputtering under a simultaneous flow of H<sub>2</sub>O vapor gas. Crystallization during sputter-deposition at elevated temperatures and solid-phase crystallization of amorphous films were compared in terms of film properties. When HAp films were deposited with Ar sputtering gas at temperatures above 460 °C, CaO byproducts precipitated with HAp crystallites. Using Xe instead of Ar resolved the compositional problem, yielding a single HAp phase. Preferentially *c*-axis-oriented HAp films were obtained at substrate temperatures between 460 and 500 °C and H<sub>2</sub>O pressures higher than  $1 \times 10^{-2}$  Pa. The absorption signal of the asymmetric stretching mode of the PO<sub>4</sub><sup>3-</sup> unit ( $\nu_3$ ) in the Fourier-transform infrared absorption (FT-IR) spectra was the narrowest for films as-crystallized during deposition with Xe, but widest for solid-phase crystallized films. While the symmetric stretching mode of PO<sub>4</sub><sup>3-</sup> ( $\nu_1$ ) is theoretically IR-inactive, this signal emerged in the FT-IR spectra of solid-phase crystallized films, but was absent for as-crystallized films, indicating superior crystallinity for the latter. The Raman scattering signal corresponding to  $\nu_1$  PO<sub>4</sub><sup>3-</sup> sensitively reflected this crystallinity. The surface hardness of as-crystallized films evaluated by a pencil hardness test was higher than that of solid-phase crystallized films.

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## 1. Introduction

Hydroxyapatite (HAp), expressed by the chemical formula of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, is the primary component material in bones and teeth. Although varieties of morphological forms of HAp, including powders, paste, scaffolding, and plates, have been provided for commercial use, the application of thin solid films still remains to be exploited for industrial and medical purposes. Major fabrication methods that have been employed so far have been plasma spraying [1], RF magnetron sputtering [2–5], facing-target sputtering [6], pulsed-laser deposition (PLD) [7–25], ion-beam assisted deposition [26], ion-beam mixing [27], sol-gel derived growth [28–31], and atomic layer deposition [32]. Of the deposition techniques conducted in a vacuum, the productivity of plasma spraying [1] is sufficiently high and hence it has been utilized to coat metallic substances with biocompatible HAp films. However, crystallinity and morphology of films coated by plasma spraying are not satisfactory. The problem common to all these deposition techniques is that the composition tends to be modified into being Ca-rich and the crystallographic orientation is quite random.

The parameters characterizing HAp thin films include their composition (the amount of OH species, completeness of the

PO<sub>4</sub><sup>3-</sup> unit, and the Ca/P molar ratio) and their crystallinity (the volume fraction of the crystallized region, the domain size, and crystallographic orientations). Against this background, our studies have been aimed at producing stoichiometric HAp films on various substrates and materials with preferential orientations. We have been employing electron cyclotron resonance (ECR) plasma sputtering to deposit HAp films. ECR plasma sputtering is categorized into remote plasma sputtering. Since the plasma source and the target are spatially separated, plasma damage to deposited films is minimized. Furthermore, continuous irradiation of deposited films with low energy ions (10–30 eV) causes intermixing of elements at the film/substrate interface, which promotes firm adhesion of the film to the substrate. Si(001) wafers were employed as substrates because these are commonly used in semiconductor technologies. There are two pathways to crystallize HAp films; the first is continuous crystallization during deposition and the second is solid-phase crystallization by post-annealing amorphous films. Which of these crystallization processes results in better crystallinity is a matter of great interest. In our previous studies, we characterized HAp films that were crystallized through post-annealing of amorphous films [33]. In the work reported in this paper, we mainly focused on HAp films that were crystallized during sputter-deposition, which enabled crystallization at lower temperatures. We clarified the difference in film properties depending on the crystallization route. Adhesion is an important characteristic when metals or ceramics are coated with HAp films

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[21,34–36]. We thus evaluated the hardness of HAp films with a pencil hardness test, which is a convenient method to judge the relative hardness between samples [37–41].

## 2. Experimental procedure

HAp films were deposited by ECR plasma sputtering. The configuration for our experimental apparatus has been described elsewhere [42,43]. A  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  target was made from HAp powders that were supplied by Ube Materials Co. The HAp powders were dissolved in a polyvinyl alcohol, concreted into a cylindrical shape to fit the target housing of the ECR sputtering apparatus, and finally sintered at a temperature within 400–800 °C by Shonan Electron Materials Laboratory. The base pressure in the deposition chamber was  $7 \times 10^{-5}$  Pa. A stainless steel bottle that contained purified water was connected to the sputtering chamber through a variable leak valve. Vapor pressure of  $\text{H}_2\text{O}$  admitted into the chamber between  $9 \times 10^{-4}$  and  $2 \times 10^{-2}$  Pa was regulated with reference to the pressure measured with an ionization gauge. Subsequently, either Ar or Xe sputtering gas was introduced and its flow rate was regulated by a mass flow controller. Then, transmitting microwaves into the plasma source generated ECR plasma and sputtering was started with applying RF to the target. ECR plasma decomposed  $\text{H}_2\text{O}$  molecules into OH, O, and H. Supplying oxygen atoms was needed to complete  $\text{PO}_4^{3-}$  units and OH species were incorporated as a component of HAp. Deposition rate was 1.3 nm/min at a  $\text{H}_2\text{O}$  pressure of 0.01 Pa. Prior to loading a 4-in. Si(100) wafer substrate into the deposition chamber, it was pretreated in a 2.5% HF solution to remove the native oxide layer. To deposit crystalline HAp films at elevated temperatures, the substrate was heated by a carbon heater from the rear side. To obtain solid-phase crystallized films, amorphous films deposited at room temperature (RT) were annealed in a rapid thermal annealing furnace (ULVAC Riko, MILA-5000) in an atmospheric  $\text{O}_2$  ambient.

The specimens analyzed in this study had thickness between 420 and 500 nm. Crystal structures of HAp films were determined by X-ray diffraction (Rigaku, RINT1500) under a Bragg–Brentano configuration with a  $\text{Cu K}\alpha$  line as the primary X-ray beam. Functional groups in HAp films were characterized by Fourier-transform infrared spectroscopy (FT-IR) (Perkin Elmer, FTIR2000) in the transmittance mode. In this case, an FT-IR spectrum of an HAp film on an Si(100) substrate and that of a bare Si(100) substrate were measured under the same deposition conditions and their backgrounds were individually subtracted. Then, a differential spectrum between the transmittance spectrum of HAp/Si and that of Si was calculated, which represented the absorption spectrum contributed only by the HAp film. Another characterization tool was Raman scattering spectroscopy/microscopy (Ranishaw, InVia Reflex). A 532-nm laser light with a power of 3 mW was focused into a spot with a diameter of less than 1  $\mu\text{m}$ . The optical system to visualize field images was confocal with the excitation laser to obtain Raman spectra. The hardness of HAp films was evaluated with a pencil hardness test following the JIS K5600-5–4 standard based on ISO 15184. A Mitsubishi Uni pencil pointed at an angle of 45° scratched the film surface for a scan length of 10 mm. Five trials were conducted for each hardness level and index of hardness (H) of the film is given as the maximum hardness of the pencil when it did not make grooves into the film.

## 3. Results

Fig. 1 shows temperature dependent XRD patterns of HAp films sputter-deposited with flowing Ar sputtering gas at  $1.7 \times 10^{-2}$  Pa.

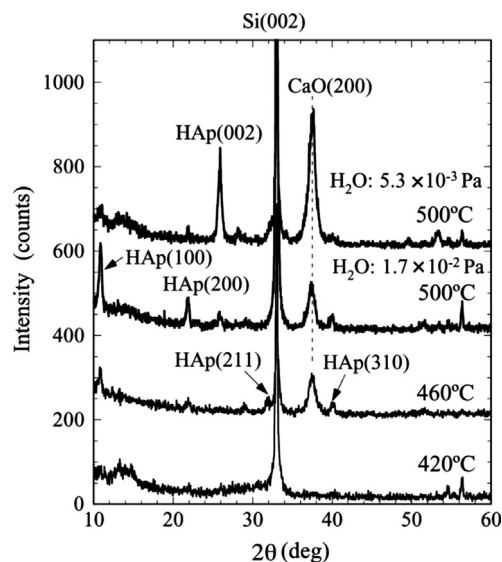


Fig. 1. XRD patterns of HAp films deposited with Ar sputtering gas at 420, 460 and 500 °C with  $\text{H}_2\text{O}$  pressure of  $1.7 \times 10^{-2}$  Pa and at 500 °C with  $\text{H}_2\text{O}$  pressure of  $5.3 \times 10^{-3}$  Pa.

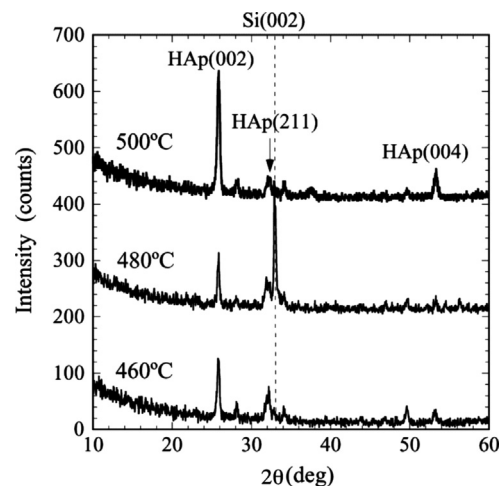


Fig. 2. XRD patterns of HAp films deposited with Xe sputtering gas at 420, 460 and 500 °C with  $\text{H}_2\text{O}$  pressure of  $1.7 \times 10^{-3}$  Pa.

The temperature of 420 °C was below the onset of crystallization in HAp films since diffraction peaks did not appear [11]. Very small HAp(211) and HAp(311) peaks, along with a broader CaO(200) peak, emerged at 460 °C. While HAp(100) and HAp(200) became the primary peaks at 500 °C, they coexisted with the CaO(200) peak. The HAp films were preferentially oriented toward the *c*-axis direction at a reduced  $\text{H}_2\text{O}$  vapor pressure of  $5.3 \times 10^{-3}$  Pa, but the CaO(200) peak intensified simultaneously. Although we examined extensive sputtering conditions including  $\text{H}_2\text{O}$  pressure and substrate temperature, we could not remove the precipitation of CaO, which meant that the composition of the HAp film inevitably became Ca-rich. Such compositional deviations toward Ca-richness [2,4,5,13,26] as well as the precipitation of CaO [25,28] are well-known phenomena.

Using Xe sputtering gas solved the compositional problem. The XRD patterns of HAp films sputter-deposited with Xe are shown in Fig. 2. HAp(002) was the primary diffraction peak for all HAp films deposited between 460 and 500 °C without the appearance of any CaO peaks, indicating that a HAp single phase film was obtained. HAp(002) as well as HAp(004) peaks were the highest at 500 °C. Since HAp films tend to be reduced while losing OH [44] when

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