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Full Length Article

Structural evolution and growth mechanisms of RF-magnetron sputter-deposited hydroxyapatite thin films on the basis of unified principles

Anna A. Ivanova[a,b], Maria A. Surmeneva[a,b], Roman A. Surmenev[a,*], Diederik Depla[c]

[a] Center of Technology, Department of Experimental Physics, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia
[b] RASA center in Tomsk, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia
[c] Research Group DRAFT, Department of Solid State Sciences, Ghent University, Krijgslaan 281/S1, 9000 Ghent, Belgium

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ABSTRACT

The structural features of RF-magnetron sputter-deposited hydroxyapatite (HA) coatings are investigated in order to reveal the effect of the working gas composition and the sample position of the substrate relative to the target erosion zone. The film properties were observed to change as a result of bombardment with energetic ions. XRD analysis of the coated substrates indicates that with the increase of the ion-to-atom ratio, the fiber texture changes from a mixed $(11\bar{2}2)+(0002)$over (0002) orientation, finally reaching a $(30\bar{3}0)$ out-of-plane orientation at high ion-to-atom ratios. TEM reveals that the microstructure of the HA coating consists of columnar grains and differs with the coating texture. The contribution of J_i/J_a to the development of microstructure and texture of the HA coating is schematically represented and discussed. The obtained results may contribute substantially to the progress of research into the development of HA coatings with tailored properties, and these coatings may be applied on the surfaces of metal implants used in bone surgery.

1. Introduction

In the field of medical material science, numerous studies have been devoted to increasing the biocompatibility of metal implants by calcium phosphate coatings (CaP), as these materials indeed have a chemical composition similar to that of the mineral component of bone [1]. Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is a typical example, belonging to the family of CaP materials [2,3].

Several methods have been applied to prepare such coatings, for example, plasma spraying, RF-magnetron sputter-deposition, biomimetic crystallization techniques, electrophoretic deposition, and sol-gel synthesis [1]. The stoichiometry of HA-based coatings, especially the Ca/P ratio, texture, and microstructure, are crucial parameters that define the properties of these biocompatible coatings. RF-magnetron sputter-deposition is a very attractive method due to the strong adherence of the coating to the substrate material, uniform thickness of the deposited layer, and the ability to control both the degree of crystallinity (amorphous or crystalline) of the coating and its Ca/P ratio [4]. These properties can be influenced by process parameters such as discharge power, chamber pressure, gas atmosphere, and substrate temperature [5–10]. A number of researchers have shown that the thermodynamic stability, reactivity, solubility, and mechanical properties of CaP coatings strongly depend on the Ca/P ratio [1,2,11,12].

Control over the preferential orientation of the HA coatings prepared via RF-magnetron sputtering may lead to the ability to tailor the behavior of the films. A number of published investigations suggest that HA coatings with textured surfaces may enable control over cellular behavior, due to the anisotropy of protein adsorption behavior on different facets of the hexagonal HA crystals [13,14]. However, this high flexibility complicates RF-magnetron sputtering, especially for the deposition of multicomponent materials. Currently, there is no reliable information on the growth mechanisms of CaP-based coatings during RF-magnetron sputter deposition. Generally, researchers focus only on the process parameters to optimize the coating properties in connection with biological studies, without investigating the fundamental aspects of film growth.

Therefore, the objective of this study was to evaluate the growth mechanism of RF-magnetron sputter-deposited HA coatings in order to gain a better understanding of the evolution of the texture and microstructure of the coatings through a combination of exper-

* Corresponding author.
E-mail address: rsurmenev@gmail.com (R.A. Surmenev).

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iments and simulations. The influence of water in the working gas atmosphere on the structural development of the RF-magnetron sputter-deposited HA coatings was studied. Additionally, the spatial arrangement of substrates in relation to the erosion zone of the target has been taken into consideration, in order to elucidate its impact on the coating characteristics.

2. Materials and methods

2.1. Thin film process conditions

HA films were deposited using a ceramic HA target by RF-magnetron sputtering (RF-generator – COMDEL, 13.56 MHz). The coatings were deposited at an RF-power of 500 W and a pressure of 0.4 Pa for 240 min. The sputter target (diameter 220 mm, thickness 9 mm) was prepared by uniaxial cold powder pressing at 70 MPa and subsequent annealing in air for 1 h at 1100 °C. The precursor powder for the target was produced by the mechanochemical activation method, with the stoichiometric composition (Ca/P = 1.67). Pure titanium (Ti, grade 2) plates of 1.5 mm thickness were used as substrates ($10 \times 10\,mm^2$). They were chemically etched in an acid solution made by mixing HF (48%), HNO_3 (66%), and distilled water in a ratio of 1:2:2.5 by volume. After acid-etching, the samples were ultrasonically washed in ethanol, followed by deionized water for 10 min at room temperature. The resulting roughness (R_a) of the treated Ti plates, as measured by atomic force microscopy, was $0.41 \pm 0.08\,\mu m$. Silicon substrates were used to evaluate the film thickness. The Si (111) wafers were ultrasonically treated in acetone, followed by ultrasonic cleaning in distilled water prior to deposition. Two series of experiments were performed. In the first series of experiments, water vapor was added to the working gas atmosphere, with the Ar/H_2O ratio of partial pressures equal to 9:1 (i.e., a mixture of Ar+10%H_2O was used). The gas pressure and the ratio of Ar and water vapor were controlled using conventional gas flow controllers.

To get a more uniform distribution of coating features, the substrate holder was rotated. The details of substrate rotation are discussed elsewhere [15]. In the second experiment, the HA coating was deposited in a pure Ar atmosphere while rotating the substrate holder. The target-substrate distance was 43 mm. The width of the target erosion zone (racetrack) was 60 mm. The samples were located on the substrate in a radial direction. The details of the target-substrate experimental setup are shown in Fig. 1. The substrate temperature during the deposition process was measured by two chromel-copel thermocouples, which were placed on the backside of the substrate holder. As the deposition time exceeded 120 min, all samples were deposited at a substrate temperature of approximately 300 °C.

2.2. HA thin film analysis

The thickness of the HA coatings deposited on silicon substrates was measured by ellipsometry ("ELLIPS – 1891 SAG" (Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences, Russia)), with a fixed angle of light of 70° in the wavelength interval λ = (250–1000) nm. The film density was measured using X-ray reflectometry (XRR), by means of a D8 Advance Bruker (Bruker AXS GmbH, Karlsruhe, Germany) instrument equipped with a scintillation detector and CuKα radiation. The samples were scanned from 0.3° to 6°, with a step size of 0.01°. Parratt's method was used to determine the critical angle of total reflection [16].

In this study, the composition and chemical states of the HA coating were analyzed using an X-ray photoelectron spectrometer (XPS) VG Scienta (Great Britain) in an ultrahigh vacuum with a pressure below 2×10^{-7} Pa. The analysis was carried out using AlKα radiation with an energy of 1486.6 eV, a power of 200 W, and a voltage of 10 kW. The obtained spectra were treated using the CasaXPS software, and the Ca/P ratio of the deposited coatings was evaluated.

X-ray diffractograms were measured on a D8 Advance Bruker diffractometer in the Bragg-Brentano configuration. The obtained diffractograms were analyzed with the program EVA. The HA (#09-0432) and titanium (#44-1294) patterns from the International Center for Diffraction Data (ICDD) database were used as references for data interpretation.

Transmission electron microscopy (TEM) of the coating cross-section structure was carried out on a JEM 2100 (JEOL Ltd., Japan) at an accelerating voltage of 200 kW and with a resolution capability of 1.4 Å at the Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences (Tomsk, Russia). Electron-transparent thin specimens for TEM were synthesized by the following methodology. ($3.0 \times 1.0 \times 0.1$) mm^3 samples were cut out of a titanium plate, using a Bühler (Isomet, Bühler, USA) precise cutting machine with a 0.3 mm thick disk and an abrasive diamond grinding agent, at a low frequency of disk rotation. The obtained billets were then treated by Ar ion thinning on the EM-09100IS (JEOL) equipment, using conditions to minimize structural changes in the samples (accelerating voltage of 6 kW, angle of incoming ion beam 2–4°).

2.3. Simulations

The simulation software SIMTRA (Simulation of Metal TRAnsport), developed by the research group DRAFT, was used to calculate the deposition profile of the coating on the substrate [17]. The model is based on the mathematical description of collisional transport of individual atoms through plasma, such that the initial characteristics, such as position, energy and direction of the generated species, are sampled from given distribution functions. The computational algorithm of the SIMTRA program is presented in Ref. [17]. The program provides a way to describe the configuration of the vacuum chamber. The geometric description of the setup specified in SIMTRA is presented in Fig. 2. Cylindrical substrates with the same dimensions ($S = 4\,cm^2$) as the samples used in the experiment were placed radially on the substrate holder.

3. Results

3.1. Growth rate and density of HA thin films

The film thickness of the HA coatings deposited on silicon substrates was evaluated by ellipsometry. The experimental growth rate was calculated on the basis of the deposition time. The dependence of the experimental growth rate (r_e) on the substrate position relative to the center of the substrate holder is shown in Fig. 3a. The growth rate in both series of experiments decreases radially from the center towards the edge of the substrate holder. In pure argon, the growth rate is maximal (2.7 nm/min) at the center of the substrate holder. When water is added to the atmosphere, the growth rate at the center of the substrate holder decreases to 1.3 nm/min. In the latter case, the film thickness becomes more uniform, as can be concluded from Fig. 3a. Indeed, the slope of the line fitted to the Ar+10%H_2O experimental data, as determined from a least squares linear regression analysis, has a more positive value (−0.006 nm/(min mm)) in comparison to the slope for the Ar-experiment (−0.021 nm/(min mm)).

It is considered that the decrease of the deposition rate due to water addition can be caused by different reasons. Important in this context is the formation of such ions as O^{2+}, H_2O^{2+}, O^+, and OH^+ and radicals by electron collision with water molecules as shown else-