

# Modification of the structure and composition of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ceramic coatings by changing the deposition conditions in $\text{O}_2$ and Ar

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**Abstract.** Hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HAp) is a material considered to be used to form structural matrices in the mineral phase of bone, dentin and enamel. HAp ceramic materials and coatings are widely applied in medicine and dentistry because of their ability to increase the tissue response to the implant surface and promote bone ingrowth and osseointegration processes. The deposition conditions affect considerably the structure and bio-functionality of the HAp coatings. We focused our research on developing deposition methods allowing a precise control of the structure and stoichiometric composition of HAp thin films. We found that the use of  $\text{O}_2$  as a reactive gas improves the quality of the sputtered hydroxyapatite coatings by resulting in the formation of films of better stoichiometry with a fine crystalline structure.

## 1. Introduction

The preparation of biomaterials for bone substitution, gene delivery and tissue engineering scaffolds applications has been the object of extensive research aimed at fulfilling the clinical requirements, namely, biocompatibility, biodegradability, mechanical and tribological stability [1]. Advances have been recently made in developing nano-crystalline hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  HAp) ceramics for orthopedic and dental applications. Orthopedic implants made of HAp and HAp-coated metal prostheses bond readily to bone and other body tissues without rejection or inflammatory reactions [2-6]. In this respect, the deposition conditions influence strongly the HAp coatings' structure, composition and capability of promoting bone regeneration [7-9]. Parameters, such as initial target

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stoichiometry [10], gas pressure, discharge power, annealing and immersion treatment conditions [11], significantly affect the characteristics of the coatings [12]. The present study's aim was to analyze the effect of the different deposition conditions on the properties of hydroxyapatite ceramic coatings.

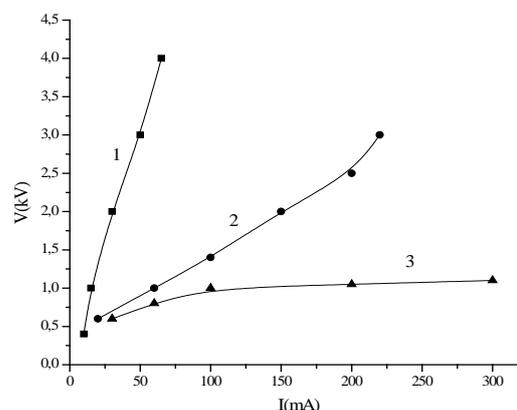
## 2. Materials and methods

Hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  films were prepared by ion-beam sputtering of a ceramic HAp target in a vacuum chamber equipped with a gridless closed-drift ion-beam source allowing the use of different reactive working gases, such as  $\text{O}_2$ , and  $\text{N}_2$  for etching, pre-cleaning and direct deposition processes [13]. The substrates were made of glass and a titanium alloy ( $\text{Ti}_6\text{Al}_4\text{V}$ ).

The operating positive anode voltage was 2,0 – 4,0 kV. The working gas pressure (mixture of  $\text{O}_2$  and Ar) was in the range  $(1 - 6) \times 10^{-2}$  Pa. The ion current was in the range 130 – 150 mA, the ion current density on the target being  $10 \text{ mA/cm}^2$ . The estimated coatings thickness was about 1.5  $\mu\text{m}$ .

Figure 1 presents the current-voltage characteristics of the ion source at various working gas pressures. At pressures  $(5 - 6) \times 10^{-2}$  Pa, a transition takes place from the discharge acceleration mode (curves' linear part) to the magnetron regime with stabilization of the current-voltage characteristics at current values above 100 mA. A pressure of approximately  $5 \times 10^{-2}$  Pa ensured optimal deposition conditions.

The structure and composition of hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  films deposited by sputtering in inert Ar and reactive  $\text{O}_2$  gases were studied by means of XRD and XPS. X-ray diffraction profiles of HAp were observed on a DRON-3 diffraction device with filtered Cu-K $\alpha$  radiation. X-ray photoelectron spectroscopy was carried out using an ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the chamber  $5 \times 10^{-8}$  Pa ( $1 \times 10^{-6}$  P during the measurements) using an Al K-alpha X-ray source (excitation energy  $h\nu = 1486,6 \text{ eV}$ ). The coating surface structure and morphology was observed by AFM (Quesant Instrument Corporation, USA) and SEM (JEM 2100).

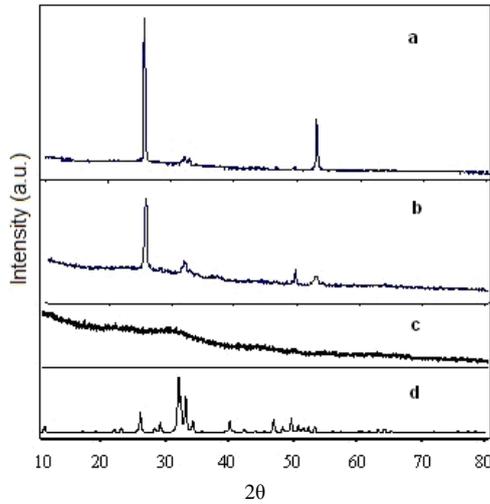


**Figure 1.** Current-voltage characteristics of the ion source at various working gas pressures. Solenoid current  $I_s = 2 \text{ A}$ ; pressure: 1 –  $p = 4 \times 10^{-2}$  Pa, 2 –  $p = 6,5 \times 10^{-2}$  Pa, 3 –  $p = 8 \times 10^{-2}$  Pa.

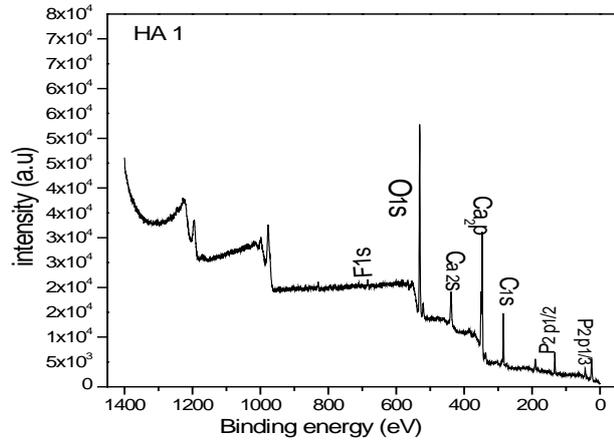
## 3. Results and discussion

The XRD patterns of the target's composition and that of as-deposited and annealed HAp coatings are presented in figure 2. The target's diffraction peaks are close to the standard HAp peak positions. The as-deposited coatings have an amorphous structure. Hydroxyapatite crystalline phases with the major HAp peaks corresponding to (002), (211), (300), (202), (310), (222), (213) reflections were observed after the as-deposited films were annealed at  $600^\circ\text{C}$  and then immersed in deionized water for hydroxyl group formation [11]. We proceeded with a structural analysis of as-deposited hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  films produced by sputtering in an inert (Ar) and a reactive ( $\text{O}_2$ ) gas. We also conducted an XPS survey scan of HAp coatings and a narrow scan of the Ca2p, P2p, O1s peaks.

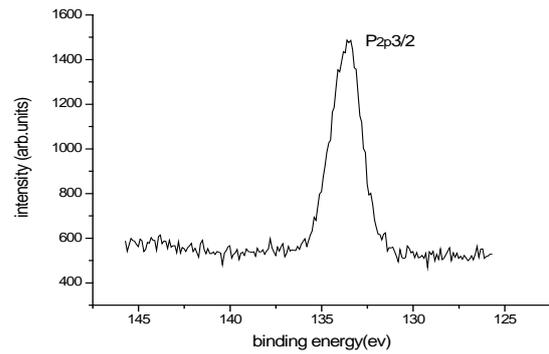
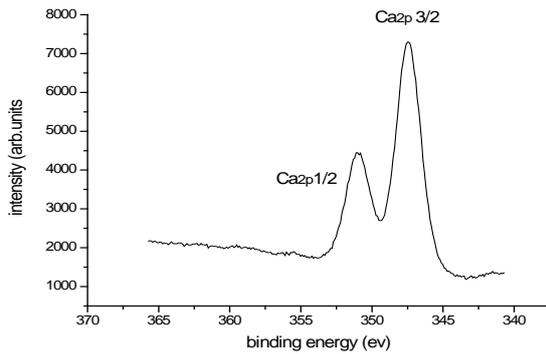
The survey spectrum shows the peaks of core-levels binding energy at about 438,7 eV related to Ca2s, 347,5 eV related to Ca2p, and 133,5 eV corresponding to P2p. The O1s peak was observed at 531,5 eV. The peak observed at about 284,6 eV is assigned to C1s and is due to surface contamination (figure 3). High-resolution XPS spectra of Ca ( $2p_{1/2}$ ), ( $2p_{3/2}$ ) and P ( $2p_{3/2}$ ) peaks are presented in figure 4. Table 1 summarizes the differences in the atomic concentrations in HAp coatings deposited in an inert (Ar) and a reactive ( $\text{O}_2$ ) gas.



**Figure 2.** XRD patterns of the target's composition and that of as-deposited and annealed HAp coatings. a – annealed HAp (O<sub>2</sub>) coating, b – annealed HAp (Ar) coating, c – as-deposited, d – target composition.



**Figure 3.** XPS survey scan of HAp coatings deposited in reactive O<sub>2</sub> gas.



**Figure 4.** High-resolution XPS spectra of Ca (2p<sub>1/2</sub>), (2p<sub>3/2</sub>) and P (2p<sub>3/2</sub>) peaks of HAp coatings deposited in reactive O<sub>2</sub> gas.

**Table 1.** Atomic concentrations of HAp coatings deposited in Ar and in O<sub>2</sub>.

HAp samples	Peak area results (atomic concentration)				Ca/P ratio
	P2p	O1s	Ca2p	F1s	
	HAp deposited in O <sub>2</sub>	14.3	59.9	24.7	
HAp deposited in Ar	13.2	58.5	26.9	1.4	2.04

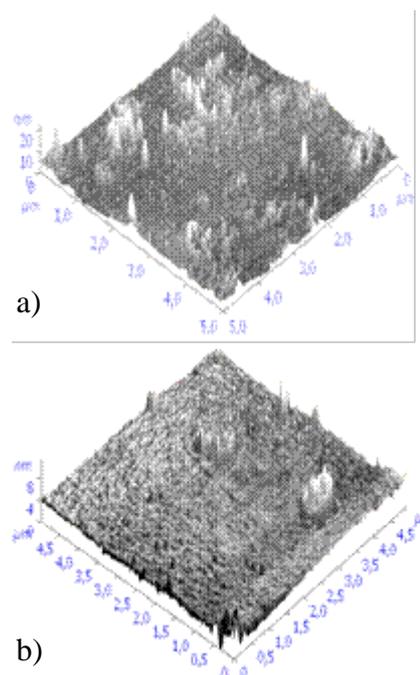
The atomic ratio percentage Ca/P was 1.73 for deposition in reactive O<sub>2</sub> and 2.04 for deposition in inert Ar. In the standard hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> composition, the calcium/phosphate ratio is 1.67. The XPS data showed a higher Ca/P ratio, which is the result of a calcium-enriched surface. The of Ca/P ratio deviation from the stoichiometric value may be due to a surface layer with a composition differing from that of the bulk material. A difference in the surface and bulk stoichiometric ratios has

also been reported in [12, 14, 15].

The SEM micrographs of HAp samples showed a well defined platelet morphology. A uniform surface structure was observed in the case of HAp coatings deposited in the reactive O<sub>2</sub> gas. The difference in the surface structure of HAp films deposited by sputtering in inert Ar and in reactive O<sub>2</sub> was revealed by AFM (figure 5). Thus, the estimated average, S<sub>a</sub> and mean-square S<sub>q</sub> roughness parameters were S<sub>a</sub> = 0,46 nm and S<sub>q</sub> = 0,73 nm for HAp coatings deposited in O<sub>2</sub>; and S<sub>a</sub> = 1.61 nm, S<sub>q</sub> = 2.18 nm for HAp coatings deposited in Ar.

#### 4. Conclusions

The results demonstrate the strong effect of the sputtering process conditions on the structural and surface properties of the coating produced, so that optimal technological deposition conditions can be recommended. The structure and composition of hydroxyapatite films deposited by sputtering in inert Ar and in reactive O<sub>2</sub> gases were investigated by XPS, XRD, SEM and AFM. The atomic ratio percentage Ca/P was 1.73 for reactive O<sub>2</sub> gas deposition and 2.04 for inert Ar gas deposition. The HAp films formed in a reactive ambient are of better quality as their surface is smoother and their composition is closer to the stoichiometric one. Varying the deposition conditions allows one to improve the quality of the sputtered hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> coatings by forming films of better stoichiometric composition with a fine crystalline structure.



**Figure 5.** Surface structure of HAp films deposited by sputtering in inert Ar (a) and in reactive O<sub>2</sub> (b) gases.

#### Acknowledgement

This research was supported by the bilateral project 2011-2013 between BAS and NASU.

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