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# Thickness dependence of crystallization process for hydroxyapatite thin films

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Hydroxyapatite (HAP) thin films (0.2 µm, 0.3 µm and 1.2 µm thickness) were grown by RF magnetron sputtering in argon atmosphere onto silicon substrates at high deposition rates (0.6 µm/h). Crystalline HAP films were obtained using a low temperature (100 °C) followed by post-deposition annealing at 300 °C, 450 °C, 500 °C and 550 °C in environmental air for 1 hour. An important influence of the films thickness upon the crystallization degree was noticed at intermediate annealing temperatures, as obtained from XRD measurements. For low and high temperatures similar values were obtained with a better crystallization degree for the thinner films. FTIR absorption led to the same conclusion considering the shape of stretching and bending $PO_4$ lines. This suggests that the crystallization process has a diffusion component besides usual thermal activation process.

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## 1. Introduction

Calcium phosphates, especially hydroxyapatite (HAP), have proved already their efficiency in the bone tissue–implant integration process in case of the new generation prostheses [1, 2]. The biocompatible coatings are crystallized either during deposition by sputtering onto heated substrates or after deposition by post-annealing in air, between 400-600 °C [3]. One can thus obtain coatings with various degrees of crystallinity and carbonatation. This is very important in case of interaction with biological fluids and cells cultures. HAP coatings with good biocompatibility were prepared by various methods such as pulsed laser deposition [4], ion beam and magnetron sputtering deposition [5]. In case of the sputtered films it is usual to prepare them at low substrate temperature and to perform post-annealing in air or air enriched with water vapours.

We have prepared amorphous calcium phosphate films of 0.2, 0.3, 1.2 µm thickness and annealed them in air at different temperatures up to 550 °C. We have noticed important influences of films thickness upon the effect of annealing process.

## 2. Experimental procedure

### 2.1 Films deposition

The calcium phosphate films were deposited by RF (1.78 MHz) magnetron sputtering onto silicon substrates at low temperature (around 100 °C). The substrates were out-gassed in high vacuum for 15 min. at 250 °C in order to improve films adhesion. The HAP target was obtained by cold-pressing followed by annealing in air at 300 °C and was cleaned for about 30 min. by sputtering prior deposition. The following deposition conditions were used: target to substrate distance: 35 mm, argon deposition pressure 0.4 Pa, deposition rate around 0.6µm/h. Three types of film to different thicknesses values were prepared: 0.2, 0.3 and 1.2 µm. For some films post-deposition annealing in air at 300, 450, 500 and 550 °C for 1 hour were applied in order to promote crystallization of HAP films. For other set of HAP films cumulative annealing at temperatures starting from 100 °C up to 510°C (100, 200, 300, 400, 450, 480, 510 °C) were performed.

### 2.2 Films characterization.

The sputtered films, before and after annealing, were measured by FTIR and XRD techniques which provide information about the short and long range order respectively. XRD measurements were performed on a Brucker diffractometer using the Cu Kα radiation ($\lambda$=0.1542 nm). FTIR measurements were performed using a Digilab 1100 FTIR spectrophotometer in the transmission mode in the range 8000-500 cm$^{-1}$. The absorption bands for the stretching region were separated in the symetric ($\nu_1$) and asymetric ($\nu_3$) vibrations using a deconvolution with Gaussian shape lines. XRD provided information about the crystallization process and the degree of crystallinity. This parameter was determined as the crystalline to whole scattered intensity ratio: $r_c = \frac{I_c}{I_c + I_a}$ where $I_c$ is the sum of the crystalline peak integral intensities, and $I_a$ is the whole pattern integral intensity, both taken after the background subtraction. The mean crystallite size was also determined from the X-ray diffraction line broadening of HAP, applying the Scherrer formula to the (002) lines, after correction for instrumental broadening. FTIR lines also offered information about the order at short-medium range and evidenced the presence of oxydril radicals or water molecules in the HAP films.

## 3. Results and discussion

### 3.1. X-ray diffraction results

The XRD patterns and the structure evolution with the annealing temperature are shown comparatively in Fig. 1, 2 for the two film thicknesses. The analysis revealed that the main crystalline phase is HAP for all films. The crystallisation process takes place somewhat differently for the two thickness values. First, the temperature at which the crystallisation occurs is bellow 450°C for the 0.3μm films and above this temperature for the 1.2 μm ones. Second, taking into account the important modification of the relative intensities of the diffraction lines compared to the isotropic HAP (e.g. PDF 9-432), we deduce that both films crystallise in an oriented manner, so that the basal plane of the hexagonal unit cell of HAP, corresponding to the (002) reflex, is predominantly parallel to the substrate. In the same time another important part of the crystallites seem to be oriented somewhat perpendicular with respect to the formers, so that some planes with indexes of type (hk0) are parallel to the surface. The thinner films have a preferred orientation of crystallites, among the (00*l*) texture discussed previously, with the (300) planes parallel to the surface, when the thicker ones have the second texture with the (210) planes predominantly parallel to the surface.

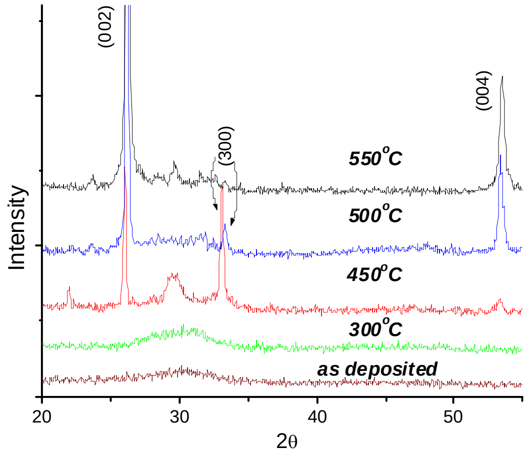

*Fig. 1 XRD pattern for 0.3 μm HAP sample.*

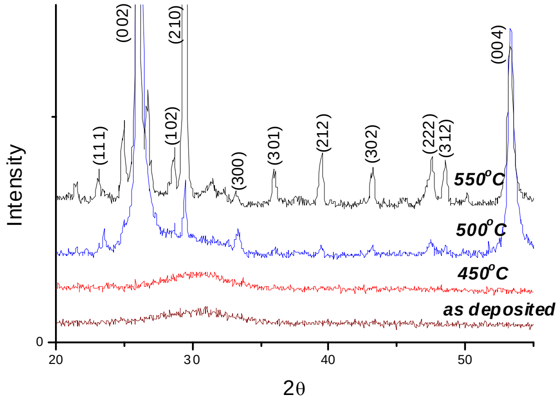

*Fig. 2 XRD pattern for 1.2 μm HAP sample.*

The degree of crystallinity of the films, as well as the mean crystallite size of HAP measured along the "*c*" crystallographic axis increase with temperature, as it could be seen in Fig. 3 and 7. The sleight decreasing of the crystallite size value of the 0.3μm film at 550 °C could be due to experimental errors, which are rather high in this range of crystallite sizes, and also could be explained as a limitation forced by the film thickness.

### 3.2 FTIR results

Fig. 4, 5, 6 displays the transmission spectra measured on the three samples after the successive annealing starting from the as deposited state up to 500 °C temperatures. One can see a continuous narrowing of the stretching and banding regions with increasing the annealing temperature appearing a clear separation of symmetrical $(\nu_1)$ and asymetrical $(\nu_3)$ vibrations at high temperatures. These suggest an increasing of the small range order (SRO) degree in the HAP films [6].

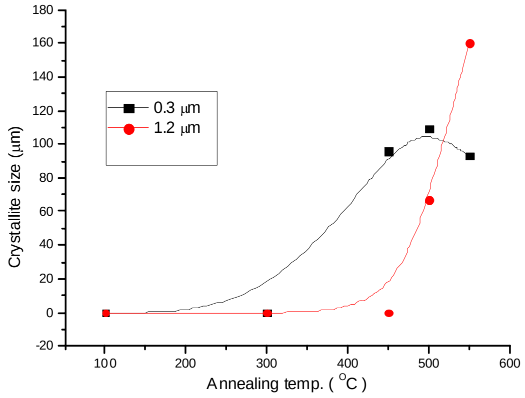

*Fig. 3. Crystallite size for the 0.3 μm and 1.2μm HAP samples.*

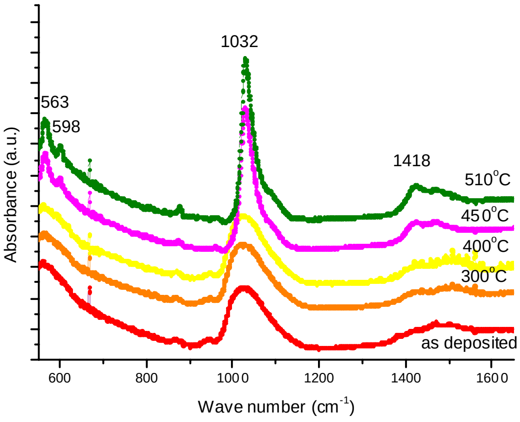

*Fig. 4 FTIR spectra for 0.2µm HAP sample.*

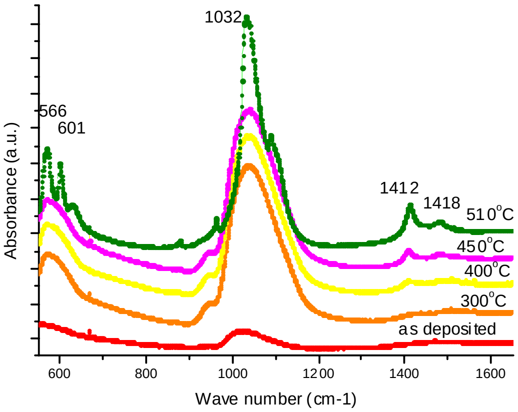

*Fig. 6 FTIR spectra for 1.2 µm HAP sample.*

One can also notice a carbonatation process of the HAP sputtered structures whose intensity increases with the annealing temperature. In our opinion this process has two components; an intrinsic one appeared during the deposition process by incorporating of CH groups from the diffusion oil, and a second one due to the diffusion of carbon dioxide molecules during annealing in environmental air. The most intense lines of carbonate groups $(CO_3)^{2-}$ were noticed in the range 1400-1500 cm$^{-1}$. The stretching absorption P-O bands (Fig. 4, 5, 6) were separated in the symmetric ($\nu_1$) and asymmetric ($\nu_3$) lines using a deconvolution with Gaussian shape lines. We have used FWHM of $\nu_3$ (1080 cm$^{-1}$) as an indicator of SRO degree as we have found it the most intense vibration in our HAP structures.

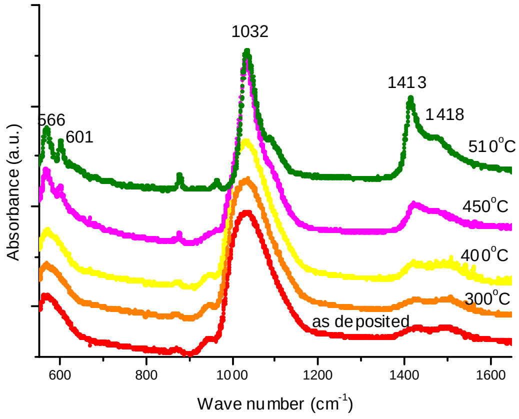

*Fig. 5. FTIR spectra for 0.3 µm HAP sample.*

Fig. 8 displays the FWHM values for $\nu_3$, asymmetrical mode for the 0.3, 1.2 µm samples annealed between 100°C and 510 °C. One can notice a generally decreasing tendency of FWHM with increasing the annealing temperature up to 500 °C. For the as-deposited samples the similar values of FWHM (63-67 cm$^{-1}$) for the three samples were anticipated due to the similar deposition conditions. The values in the range of 12-14 cm$^{-1}$ for the maximum annealing temperature suggests a similar degree of SRO for the 0.3 µm and 1.2 µm samples. This is concordant with the XRD results which showed that 1h annealing at 500 °C in a single step process produced similar crystallization degrees of FWHM for the three studied samples. Between as-deposited state and 500 °C annealed one, the decreasing tendency depends on films thickness. At intermediate annealing temperatures we have obtained very different values of FWHM for the three samples. For the thinnest ones (0.2, 0.3 µm) the FWHM values have a slow, round shape decreasing starting from temperatures of 200 °C while the thick sample display a constant value for FWHM up to 450 °C and than has a steep decreasing between 480-500 °C.

Because the annealing conditions were identical for the three samples the differences in the FTIR spectra could be due to the differences in the films thickness values. During the sputtering process it is expected to obtain calcium phosphate nonstoichiometric layers poor in volatile compounds such as oxygen and hydrogen atoms. In order to restore HAP crystalline structure in the sputtered films it is necessary to recover films stoichiometry during the annealing process. From this reason we have chosen annealing in environmental air which contains oxygen but also water molecules which can diffuse into the HAP structures at high temperatures. It is known that the diffusion lengths of one the molecular species are strongly increasing with the annealing temperature.

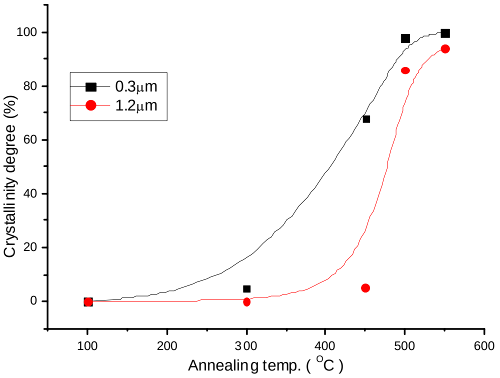

*Fig. 7. Average crystallinity degree for 0.3µm and 1.2µm HAP samples; (the lines for visual help).*

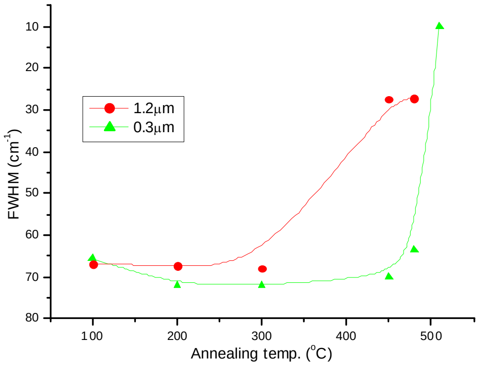

*Fig. 8. FWHM values for $\nu_3$, asymmetrical mode for the 0.3 µm and 1.2 µm; (the lines for visual help).*

We can explain the obtained results supposing a diffusion length of diffusing species at 200-300 °C of around 0.1 µm. This value is the same order with the thickness of the 0.2, 0.3 µm samples, and negligible respect to the 1.2 µm sample. At high temperatures, up to 450 °C, the diffusion length is increasing over the thickness of HAP samples, being comparable with most thick sample. One can explain why all the HAP samples displayed the same crystallinity degree at 550 °C, while at 450 °C the crystallinity degree depends on the thickness of HAP samples.

## 4. Conclusions

Using magnetron sputtering technique we have prepared HAP films (Ca/P ratio 1.4) of three thickness values, 0.2, 0.3, 1.2 µm, in order to study the structural modifications induced by annealing in air between 100 °C and 550 °C. These modifications were estimated from the crystallinity obtained by X-ray diffraction measurement and by FWHM of $\nu_3$ streaching line obtained from FTIR measurements. For the as deposited samples which are amorphous in XRD we have obtained similar FWHM values for the three samples. For annealing temperatures higher than 500 °C the crystallinity degree is higher than 90% for all samples and the FWHM values in the range of 10-12 cm$^{-1}$. At intermediate temperatures the effect of annealing is strongly dependent on the film thickness, maximum value of crystallinity being obtained for the thinnest films. This behaviour could be explained considering that a prerequisite component in the crystallization process is the recovering of stoichiometry performed by the diffusion of the oxygen and water molecules from environmental air.

## Acnowledgements

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