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PHENOMENOLOGICAL MODEL OF A CALCIUM-PHOSPHATE COATING GROWTH WITH TAILORED PROPERTIES

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The properties of radio-frequency (RF) magnetron sputter deposited calcium-phosphate (CaP) coatings are reported. It is revealed that the coatings chemistry, molecular and phase composition are strictly dependent on the deposition conditions such as RF-power, negative substrate bias on the substrate, deposition time, and sample position on the substrate relative to the target erosion profile [1-6]. Powders of hydroxyapatite (HA) and Si-substituted HA (SiHA) ($Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$, x=0; 0.5 and 1.72) were prepared by mechanochemical activation method at the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences (ISSC SB RAS) and had an average particle size of ~70 nm. The targets for sputtering were prepared via a ceramic technology [7]. The following substrate materials were used: stainless steel 316L, Ti, NiTi, magnesium AZ31 and AZ91 alloys, Al_2O_3-ZrO_2 and polytetrafluoroethylene PTFE [6, 7].

Based on the results of X-ray diffraction, IR spectroscopy, X-ray photoelectron spectroscopy, etc a phenomenological model was developed and presented in Figure 1. The model allows to prepare a CaP coating with tailored properties (texture, structure, phase composition, and the Ca/P ratio).

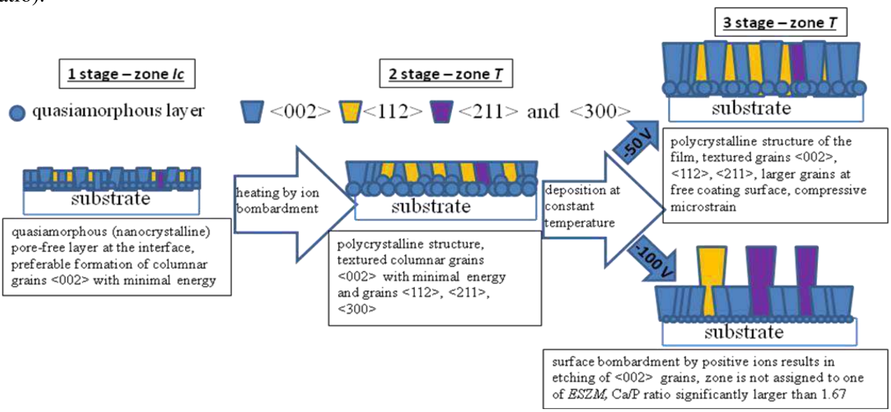

Fig. 1. A phenomenological model for the formation of RF magnetron sputter deposited CaP coating at the negative substrate bias (also at the substrate heating) and low power density: maximal energy of positive ions without taking into account V_p at the bias -100 V ~ 100 eV, substrate temperature (160 – 200) °C, ions flux density from plasma at the bias -100 V ~ $4{,}6\times10^{14}$ particles/($cm^2\cdot s$), at the bias of -50 V ~ 1.45×10^{14} particles/($cm^2\cdot s$)

The direct measurements of the ion current to the substrate depending on the deposition conditions allowed to calculate the ratio of the flux of ions to atoms and correlate this value with the texture, structure and the Ca/P ratio, which determines the phase composition of the coatings as well as their bioactive performance (Table 1). It is revealed that growth conditions on the condensation surface at a low power density do not allow obtaining coatings of crystalline HA, and significant deviations from the stoichiometry are characteristic of the case of high energies of positive ions, of the order of 100 eV, bombarding the coating growth surface. Only deposition conditions at a high RF-power resulted in the crystalline HA coatings with the Ca/P ratio close to that of stoichiometric HA.

Characterization of the deposited CaP-based coatings at a low RF-power level allows revealing the specific surface structure, which has irregular grain-like morphology. This structure depends on the samples arrangement on the substrate facing the erosion zone of the target at a high substrate bias of -100 V, which defines decreased atomic flux from the target compared with higher power densities. This surface structure was not previously described in any of existing structure zone models (*SZM*s), e.g. described in details by A. Anders [8]. We have done an analysis and calculated the substrate temperature relative to the melting temperature of HA (T_m=1923 К). As a comparison model, a well-known SZM model by A. Anders was used. A new surface structure of the CaP coating is developed under the following CaP coatings deposition conditions such as a low RF-power level, $T_{deposition}$=(160 – 200) °C, i.e., T/T_m <(0.225 – 0.246), positive ions energy ~ 100 eV. Thus, in the case of depositions at low RF-power level, the structure of the coating surface was established, which extends the well-known structural zone models (Thornton, Monsieur, Movchan and Demchishin, Anders, etc.).

Table 1. The relationship between the microstructure of RF magnetron sputter deposited coating on the condensation surface and deposition conditions

Power density, W/cm^2	Bias, V	Maximal ions energy, eV	Density of ions flux, ×10^{14} particles/(cm^2·s)	Average deposition rate, nm/min	Chemical formula or the Ca/P ratio
1.32	grounded	-	3.02	5.5	Coating growth with the HA structure and texture <001>, $(Ca_{10}(PO_4)_6(OH)_{2-2x}O_xV_x$, where V–vacancy (0<x<1)), the Ca/P ratio ~1,6 – 1,7, substrate temperature (200 – 310) °C. Higher values of microstress at the bias
	-50	50	8.54	5.6	
	-100	100	11.5	5.7	
0.14	grounded	-	0.66	0.95	Coating growth with the structure of low crystalline HA, the Ca/P ratio increases with the increase of the bias, moreover Ca/P>1,7 which does not depend on the working gas atmosphere, substrate temperature (160 – 200) °C. More effective coating sputtering with the increase of the bias
	-50	50	1.45	0.89	
	-100	100	4.6	0.81	

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