Hafnium dioxide obtained by Atomic Layer Deposition – the ability to support the formation of biological apatite

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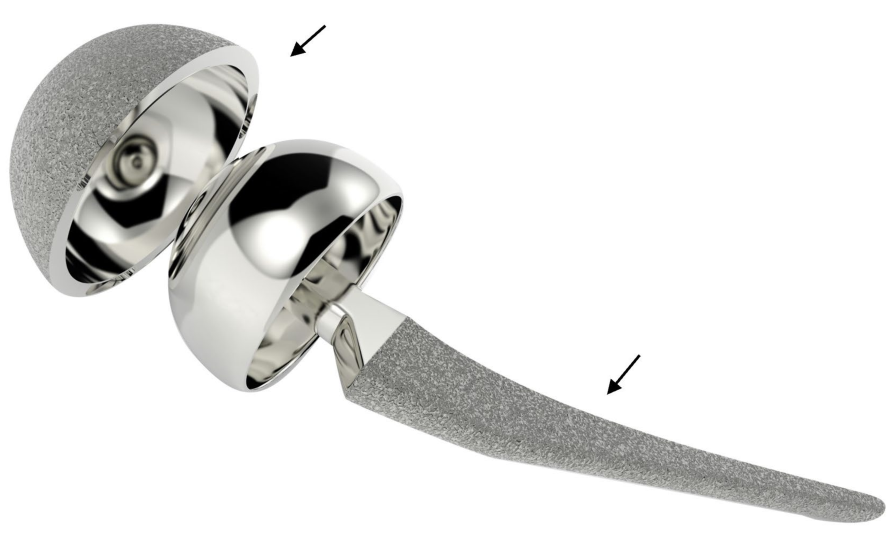
Abstract:

The implant as a scaffold for defected bone tissue plays, particularly, a mechanical role. The ability of bone tissue to rebuild and regenerate is the basis for implant integration, i.e., regaining the mechanical properties the treated part of the skeleton. Durability, stability, and long-term strength of the bone-implant connection determined the research developed the functionality of implant surfaces. The implant coatings are the main solution to support the implant osteointegration. Presented result has showed that HfO_2 film deposited by the Atomic Layer Deposition (ALD) technique supports actively the nucleation of biological apatite precursors. It has been also pointed out the similarity with the osteogenesis phenomena occurring in the nature. The nucleation of biological apatite precursors has been occurred in form of spherical structures with well-developed morphology. The oxygen atoms from the HfO_2 coating actively participate in the forming of the amorphous phosphate calcium. Moreover, the structures spontaneously absorbed trace amounts of Mg^{2+} ions. Presented experiment has confirmed that HfO2 obtained by ALD technology possess the ability to spontaneously captur of chemical elements crucial in bone mineral fraction, among others Ca, P, and trace elements Mg. The result indicate the applicability of HfO_2 obtained by ALD for personalized traumatology medicine.

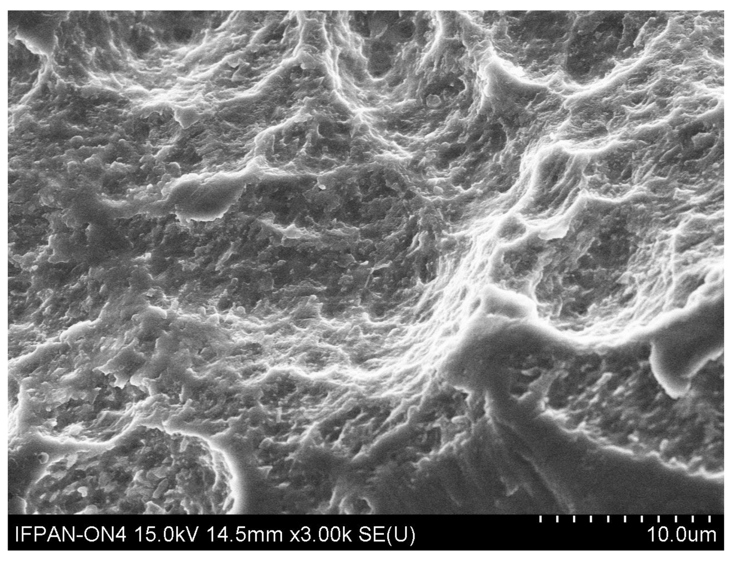
Atomic Layer Deposition (ALD) for implantology:

The ALD technology is based of sequential pulses of reagents to the reaction chamber, each separated by purge by an inert gas, e.g. nitrogen or argon. Using the ALD technique, it is possible to obtain homogeneous layers on large surfaces.

Implantological treatments of defected bone are nowadays a standard procedure recognized by a traumatology medicine. The bone cells prefer rough and porous surfaces. The implant surface geometry in micro and in nano scale has a significance for the osteocells proliferation, adhesion, so with the ingrowth with the implant surface. The implant coating has to reflect the porosity and roughness of the matrix. The main attribute of ALD technology is atomic layer by layer growth of thin films. As a result, thin films are fabricated which covered tightly and **conformal** the matrix. The inseparability bonding with the surface of deposited thin films results in safety of use.



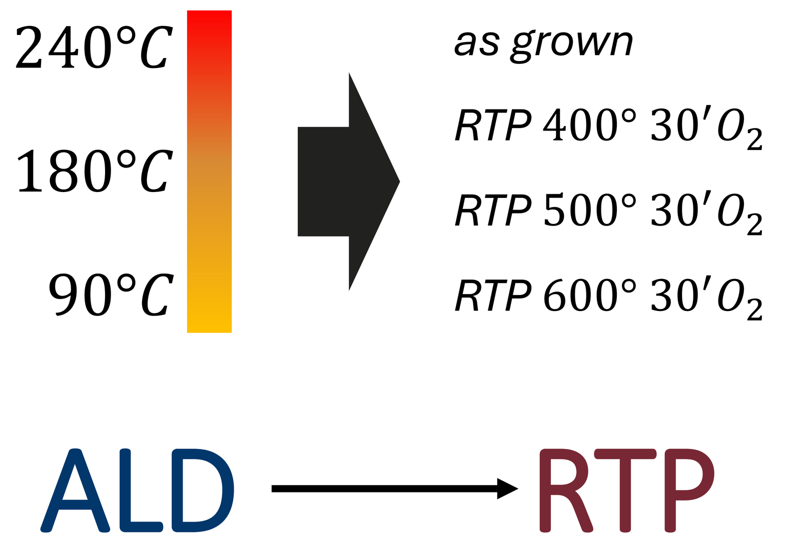
Hip bone implant with marked porous zones for bone ingrowth.



SEM image of the porous implant surface covered with ALD method.

Hafnium dioxide films:

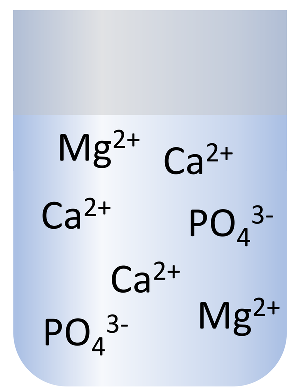
The HfO_2 ALD thin films were prepared in the Savannah-100 Cambridge NanoTech reactor. Purging phases were preceded by nitrogen.Tetrakis(diethylamido)hafnium (TDMAH) and deionized water were used as a metal and as an oxygen precursor, respectively. The growth temperature varied between 90°C and 270°C. The films were annealed with RTP after ALD growth. The RTP processes were caried out in oxygen atmosphere at the temperature 400°C-600°C.



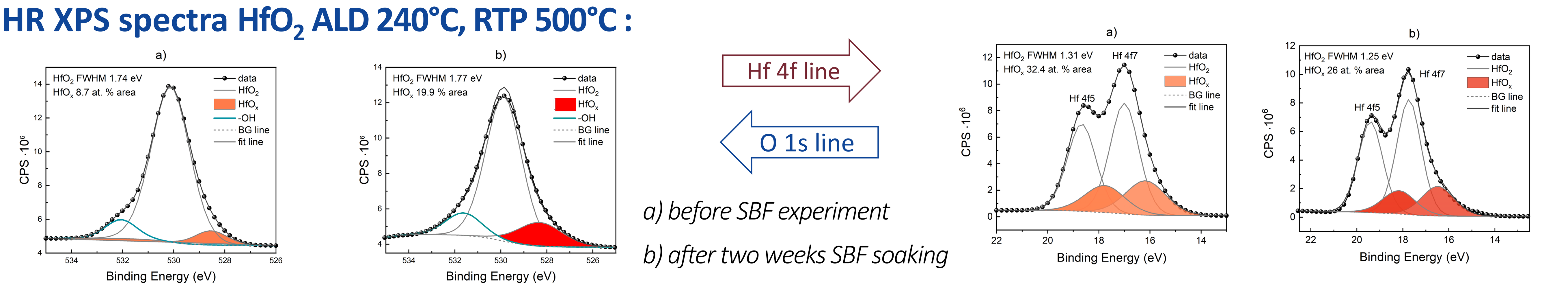
Simulated Body Fluide (SBF):

SBF experiment was performed according to standard ISO 23317-2014. SBF method was developed by Kokubo et al.[1] for tests the self- creation of bone like BAp on the surface, based on ions solution imitating a human blood plasma. SBF is a useful tool for tests the biological activity of materials. Moreover, it allows to reduce the number of experiments with the use of living cells (*in vitro*) and above all laboratory animals (*in vivo*). The commonly long bone implants, e.g., hip bones' are made from metals. The SBF experiment is also challenging test of the materials' durability, especially for those one pretending to be leaky since biological environment is classified as aggressive for metal surfaces.

[1] T. Kokubo and H. Takadama, "How useful is SBF in predicting in vivo bone bioactivity?," Biomaterials, vol. 27, no. 15, pp. 2907–2915, May 2006



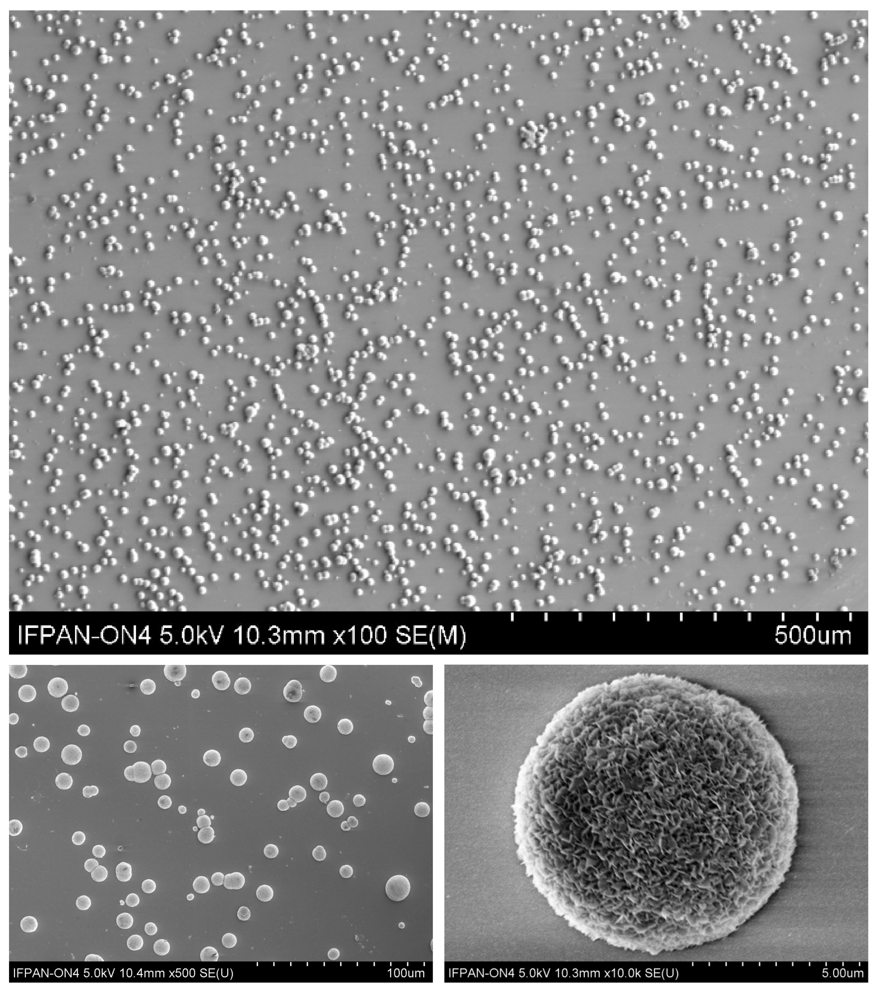
HR XPS spectra HfO_2 ALD 240°C, RTP 500°C :



If compared the samples both as grown and after RTP treatment (not shown here) stands out the presence of nonstoichiometric fraction of HfO_2. The HfO_x were detectable as well by O 1s line as Hf 4f line after RTP procedure which ensure free bonds by Hf atoms. The nonstoichiometric components lines increased also due to SBF experiment both Hf 4f as well as O 1s. [3]

Oxygen atoms have been participated actively in the nucleation of the ACP structures what would be crucial attribute providing the mechanical resilience of BAp adhesion to ALD thin films of HfO_2.

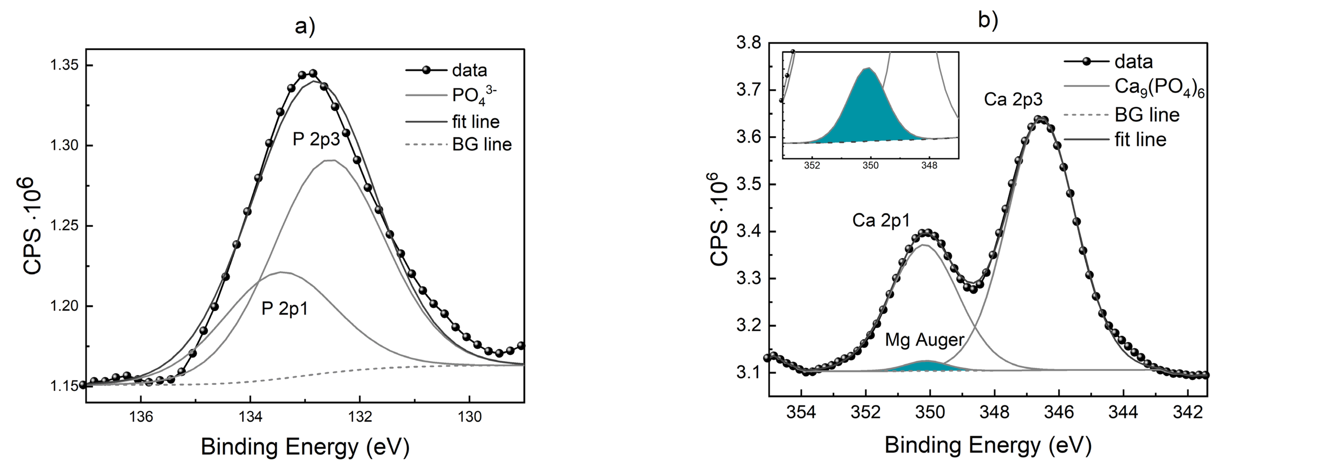
SEM results:



- HfO_2 deposited by ALD at 240°C and annealed by RTP at 500°C 30' in oxygen atmosfere posses the ability to nucleate theamorphous calcium orthophosphate (ACP),
- The spherical structures of ACP cover homogenously the whole surface,
- ACP is a precursor of BAp in natural occured biomineralization phenomenas. [2],
- HfO_2 films **mimic** the bone matrix biomineralization

Spontaneous acquisition of trace elements from the physiological environment:

Fitting simulated lines to the experimental data of the Ca 2p line from sample HfO2 ALD 240°C, RTP 500°C confirmed the spin-orbit splitting line with the 2p 3/2 BE 346.3 eV but an additional line with BE close to 350 eV) considerably improved the fitting. This value is similar to the one very intense reported for Mg Auger line with the BE 351.67 eV.



Bone tissue is the basic structural unit of the skeletal system, but also an endocrine organ. Inorganic bone tissue component is a specific reservoir of trace elements mandatory to maintain the body's homeostasis Spontaneous replenishment of the reservoir by capturing trace elements from body fluids is a natural process in vertebrates. The presence of Mg2+ ions provide powerful connection between implant surface and bone tissue..

[2] A. Lotsari, A. K. Rajasekharan, M. Halvarsson, and M. Andersson, "Transformation of amorphous calcium phosphate to bone-like apatite," Nat Commun, vol. 9, no. 1, Dec. 2018

[3] B. V. Crist, Handbooks of Monochromatic XPS Spectra. 3408 Emerald Drive, Ames, Iowa, 50010 USA: XPS International, Inc., 1999.

Conclusions:

The HfO_2 grown by ALD and post deposited annealed with the RTP possess two crucial attributes to become an implant coating mimicking the natural phenomena. Firstly, HfO2 obtained by ALD initiates ACP nucleation, secondly simultaneously builds in the trace elements like Mg from the physiological fluids.

Physical and chemical characterisation of the films while the technology optimalisation was an integral component of the research. Complementary approach allowed to achieve the functionality of biomaterials with the maintaining the films quality. The finding possess significance for future progress of personalized traumatological medicine.

A particular strength of the approach is that HfO_2 is able to mimic the biological phenomena through the indicating the BAP nucleation. Moreover, spontaneously incorporating trace elements such Mg, crucial for ensuring the homeostasis of bone tissue and the body.