

## An Overview of Sputtering Hydroxyapatite for Biomedical Application.

SS Oladijo<sup>1</sup>, ET Akinlabi<sup>1</sup>, FM Mwema<sup>1,2</sup>, Artemis Stamboulis<sup>3</sup>

<sup>1</sup>Department of Mechanical Engineering Science, University of Johannesburg, South Africa

<sup>2</sup>Materials, Design & Manufacturing Group (MADEM), Department of Mechanical Engineering, Dedan Kimathi University of Technology, Nyeri, Kenya.

<sup>3</sup>University of Birmingham, Birmingham, United Kingdom

### Abstract-

Materials such as biocompatible metals, ceramics, composites, and polymers are used in the fabrication of biomedical implants which are used in the human body especially for the replacement of hard tissues. However, they degrade with time since they are subjected to different mechanical conditions and long-term exposure to fluids corrosion. Therefore, to curb these limitations, the surface properties are usually coated with thin metallic and nonmetallic materials. One such nonmetal is Hydroxyapatite (HA) coating which has the potential of mitigating these shortcomings and it is a biocompatible and bioactive material. This paper provides an overview of the existing literature on the sputtering of hydroxyapatite coating for biomedical applications with emphasis on the deposition conditions and parameters

**Key words:** Magnetron sputtering, Hydroxyapatite (HA), Biomedical material, Corrosion, Thin films coating

### 1. Introduction

A biomaterial is an essential material that is used and adapted for biomedical applications [1]. They are synthetic or natural material intended to function appropriately in a bio-environment for use in the human body [2]. Therefore, the selection of biomaterials plays a key role in the design and development of biomedical product. The materials commonly used as biomaterial are metallic, polymeric and ceramic materials. Stainless steels, titanium, and its alloys, and Co-Cr alloys are examples of metallic materials which find applications as implants. Metals have excellent mechanical properties as compared to the other group of materials. Mechanical strength is very important in implants since they are commonly used for (i) load-bearing implant and (ii) internal fixation devices. However, metals degrade with time when they are subjected to different mechanical conditions and long-term exposure to fluids. Polymeric materials such as synthetic collagen, TEGDMA, glucosaminoglycans, acetal, silicone, ultrahigh-molecular-weight-polyethylene, polymethylmethacrylate provide a wide range of bulk composition and physical properties in implant while some are biodegradable, and therefore can be used for applications where it is desired to deliver a specific function for a temporary period. Although, they have poor mechanical strengths which makes them undergo mechanical wear and breakdown [2]. Ceramic materials such as calcium phosphate, zirconia, alumina, bioactive glass are inorganic compounds of metallic or nonmetallic material. They possess excellent bioactivity in body environments and facilitate easy cell growth. Ceramics are limited by poor mechanical property which restricts their bulk use in high load-bearing conditions [3][4].



Therefore, to curb these limitations, depositing porous ceramics coating on metallic substrates has advantages of both materials hence gives mechanical stability and excellent biocompatibility to the bio implant. In recent years hydroxyapatite (HA) has become the first choice for coating bio-implants due to its bioactive properties and its chemical structure, which is almost similar to the human bone [5]. Hydroxyapatite is coated on metallic substrates to keep the mechanical properties of the metal such a load-bearing ability and, take advantage of the coating's chemical similarity and biocompatibility with the bone [6].

Hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  is one of the most stable and less-soluble calcium phosphate bioceramics with Ca/P ratio of 1.67, it has the best bioactivity among all form of calcium phosphate and can bond directly onto bone [7][8][9]. HA has better stability when compared to other calcium phosphates. Thermodynamically, hydroxyapatite is the most stable calcium phosphate compound under physiological conditions as temperature, pH, and composition of the body fluids [10]. It has excellent properties such as biocompatibility, bioactivity, osteoconductivity, non-toxicity, and inflammatory nature [8]. HA structure commonly found belongs to the hexagonal system with space group P63/m, revealing symmetry perpendicular to three equivalent 'a' axis (a1, a2 and a3), which form angles of  $120^\circ$  to each other. HA unit cell is composed of calcium (Ca) and phosphates and may be represented by  $\text{M}_{14}\text{M}_{26}(\text{PO}_4)_6(\text{OH})_2$ , in which the crystallographic positions of its M1 and M2 are two differences for 10 calcium atoms. Four Ca atoms are surrounded by nine oxygen (O) atoms of the phosphate groups at the M1 position, belonging to the  $\text{PO}_4$  tetrahedron. Six other Ca atoms are surrounded by the remaining six O atoms and one of the two OH [9], as shown in Figure 1 below.

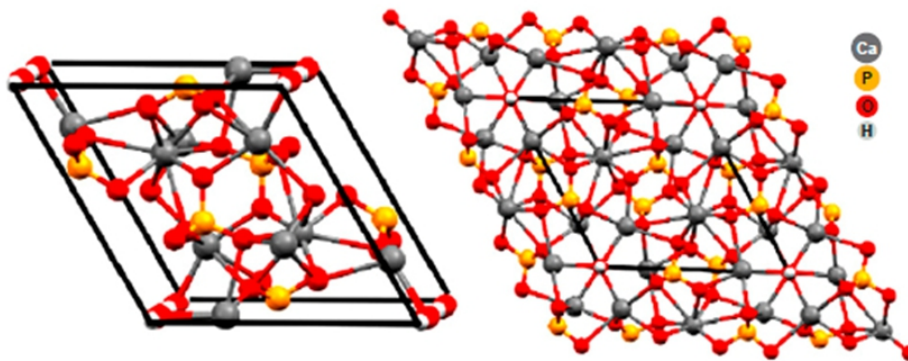


Figure 1: Crystalline structure of the hydroxyapatite (left) and the projection of the HAP structure in plane 001 (right) [9].

HA coatings have been deposited by various method, some of which include plasma spraying [11], thermal spray [12], sputtering [7], pulsed laser deposition [13], dip coating [14], sol-gel [15], ion beam assisted deposition [16] and electrophoretic deposition [17].

Mohseni et al. [18], and Surmenev et al. [19] reported various advantages and disadvantages of the hydroxyapatite coating for biomedical applications due to the restriction imposed by

clinical uses. However, despite the advantages of all the deposition techniques, their most essential limitation is the difficulty to control the phase and chemical composition of a Ca/P coating. It is of no doubt that RF-magnetron sputtering allows controlling the properties of Ca/P films within a rather wide range and forms a dense, good adhesion at the interface between the coating and the substrate, uniform coating to devices with complex configurations with uniformity in thickness, composition and the ability to coat implants with difficult surface geometries [20]. Furthermore, sputtering is a vital and prominent procedure among the physical vapor deposition (PVD) processes [21]. As shown in Figure 2, o90yg is a diagram of the magnetron sputtering mechanism which involves the sputtering of HA target and its interaction of ions with the surface of the substrate. The basic steps of the sputtering process are [22].

- (i) the neutral gas is ionized by an external power supply, producing a glow discharge or plasma
- (ii) a source (the cathode, also called the target) is bombarded in high vacuum by gas ions due to the potential drop acceleration in the cathode sheath;
- (iii) atoms from the target are ejected by momentum transfer and diffuse through the vacuum chamber;
- (iv) atoms are deposited on the substrate to be coated and form a thin film.

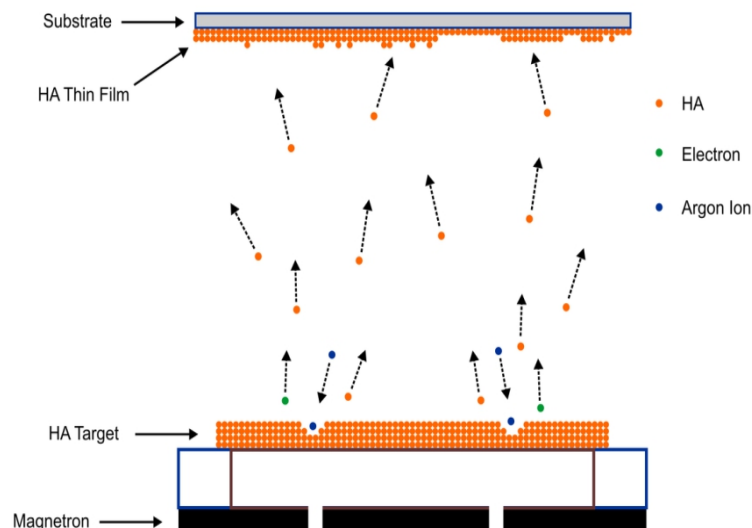


Figure 2: Schematic diagram of the sputtering mechanism [6].

As shown in Figure 2, sputtering deposition is influenced by various parameters including power, argon flow rate, working pressure, substrate temperature, and target composition [23].

These parameters further play an important role in determine the quality of the HA coating. Hence, most researchers are interested in understanding the influence of these parameters, as single or combination of these parameters. The purpose of this paper is to undertake an overview of the HA sputtering with an emphasis on the influence of sputtering/deposition parameters on the quality, deposition process, and mechanism of formation of HA coatings. The article serves as an important resource towards optimization studies of HA deposition for biomedical implant applications.

## 2. Overview of HA deposition

There are many factors which influence the hydroxyapatite coating, such as substrate temperature, deposition parameters, and post-processing treatment [24]. Table 1 shows the overview of factors influencing Hydroxyapatite coating from previous studies.

Table 1: Overview of factors influencing Hydroxyapatite coating.

Target; Substrate /Ref	Method of deposition	Aims of research	Deposition parameters	Results	Remarks (Literature gaps; the new direction of research)
HA-Ag; Ti-6Al-4V /[25]	Radio frequency and Direct Current Magnetron sputtering	To investigate the effect of deposition temperature and target-substrate distance on (i) the structure, phases, (ii) mechanical and (iii) tribological properties of multi-layer HA-Ag coatings.	(i) Distance between target and substrate (D) = 4 cm, 6 cm 8 cm; (ii) Substrate temperature varying from room temperature (RT) to 200°C; (iii) Powers = 600 W RF and 20 W DC; (iv) bias voltage = -20 V; (v) Argon gas flowrate 99.9% purity; (vi) Working pressure = 0.5 Pa.	(i) The energy dispersive spectroscopy (EDS) result showed the Ca/P ratio increased while deposition distance increases; (ii) The coating tribological behavior in simulated body fluid solution at 37°C showed higher friction coefficient at 200°C and less wear rates to those coated at RT; (iii) The atomic force microscopy (AFM) result showed roughness increased due to increase in temperature and reduced due to increase in distance; (iv) The coating crystallite size obtained increases by 13% and 72% respectively at 4 cm and 6 cm when the temperature was increased from RT to 200 °C	An optimization study on power, substrate temperature, and the distance between target and substrate on the crystallinity characteristics are necessary.
HA; Quartz /[26]	Radio-frequency magnetron sputtering	To investigate the effect of (i) thickness on optical and (ii) microwave dielectric properties of Hydroxyapatite films deposited by RF magnetron sputtering	(i) Distance between the target and the substrate = 6 cm; (ii) RF power = 50 W; (iii) depositions time duration = 60, 80, 180 and 520 min; (iv) pressure= 7 x 10 <sup>-3</sup> Torr; Argon gas = 99.999% pure; (V) Films of thicknesses 300 ± 10, 400 ± 10, 1000 ± 12, and 3000 ± 15 nm were	(i) Structural and microstructural analysis obtained from X-ray diffraction (XRD) result revealed amorphous as-deposited films and improvement in the crystallinity after annealed at 700 °C for 2 h; (ii) crystallinity of the coatings improved significantly with increased in the deposition time; (iii) The estimate of the strain obtained through XRD patterns using uniform deformation model (UDM) showed the increase in the thickness, lead to the residual strain that caused a shift in the peaks; (iv) Unit cell volume	Characterization of the tribological study should be included in the future study to evaluate the resistance of the film to sliding loads. This is important for evaluating its mechanical stability.

			produced; (vi) annealed in air at 700 °C for 2 h	and average crystallite size increased with the increased; whilst the non-linear absorption coefficient decreased with the increasing thickness of the HA film; (v) The EDS analysis revealed the presence of Ca, P, and O with Ca/P ratio of 1.58 in the HA coating.	
HA-ZrO <sub>2</sub> ; titanium sputtering / [27]	Magnetron sputtering	To investigate the mechanical properties of hydroxyapatite-zirconia coatings prepared by magnetron sputtering	(i) Base pressure = $2 \times 10^{-3}$ Pa; (ii) sputtering power = 200 W; (iii) argon with purity of 99.99%; (iv) deposition time = 3 hrs; (v) working pressure = 0.1 MPa; (vi) After, tempered at 600 °C for 2 hrs	(i) An increase in HA content improved the surface morphologies, and increased the contact area of the coating surfaces; (ii) The residual stress analyses obtained from XRD showed that an increased in the HA content reduce the residual stresses of the composite coatings; (iii) The EDS analysis indicated that the coating surface is mainly the chemical elements of HA, and the other trace elements are slightly changed, which does not affect the mechanical properties of the coatings; (v) Adhesion automatic scratch tester result showed that the bonding strength of 50HA±50ZrO <sub>2</sub> composite coating is 30 N, whereas that of 75HA±25ZrO <sub>2</sub> composite coating is 17.5 N.	It would be interesting to study the relationship between the residual stresses and the bonding strength of the coating
HA; Ti-6Al-4V / [28]	Radio-frequency (RF) magnetron sputtering	To investigate the effect of thermal treatment on (i) structure, phase and (ii) mechanical properties of hydroxyapatite thin films grown by RF magnetron sputtering	(i) Sputtering power = 600 W; (ii) time = 5 hrs; (iii) distance between the substrate and the target = 80 mm; (iv) bias voltage = -30 V, -25 V and -20 V; (v) Argon gas = 99.99% of purity (vi) heat-treated at 400 °C and 700 °C for 2 hrs in argon atm.	(i) Profilometer result showed that an increased in the bias voltage leads to the densification of coating and decrease in the film thickness; (ii) The hydroxyapatite thin film without heat treatment cross sectional view result obtained from the SEM showed a dense and compact coating; (iii) The X-ray diffractogram result for the hydroxyapatite and the coatings showed a change in preferential growth between the hydroxyapatite and the deposited coatings; (iv) Crystalline size and Full Width at Half Maximum for the coatings obtained as a function of the annealing temperatures showed increased in the crystallite size with thermal treatment application by 38% and 43% for hydroxyapatite 400 °C and 700 °C respectively; (v) Hardness and Elastic modulus result obtained showed that the H and E values of hydroxyapatite thin film on the Ti-6Al-4V increased respectively by 5% and 9% from the hydroxyapatite coating without heat treatment to the hydroxyapatite 400 °C samples and, decreased to the lowest value at 700°C	The relationship between the Elastic modulus and Hardness obtained for hydroxyapatite coating without heat treatment and hydroxyapatite coating heat-treated at 400 °C and 700°C is inconclusive due to the limited number of data hence more temperature range needed to be considered in the future study
Si/HA; Titanium	Radio frequency magnetron	To investigate the effect of silicate	(i) RF power = 500 W; (ii) working pressure = 0.4 Pa;	(i) FE-SEM result shows Si-HA coatings morphology was granular-like with poles apart	(i) The surface topography

/[29]	sputtering	doping on the (i) structure and (ii) mechanical properties of thin nanostructured RF magnetron sputter-deposited hydroxyapatite films	(iii) base pressure = $10^{-4}$ Pa; (iii) distance between the substrate and the target = 40 mm; (iv) time = 8 hrs	grain shape and size; (ii) Poles apart surface morphology was found due to presence of silicon in the films; (iii) Grain sizes decreases due to increase in silicon content; (iv) The XPS revealed that the calculated Ca/(P + Si) ratios of $1.49 \pm 0.01$ and $1.05 \pm 0.02$ determined for coating of Si-HA powder containing of 1.2 and 4.6 at.% Si was lower to the theoretical ratio for Si-HA (Ca/(P+Si)=1.67); (v) The profilometer result showed increased in surface roughness after depositing hydroxyapatite coating and decreases when silica content.	regardless of the chemistry required attention to increase the osseointegration process;
HA; Ti6Al4V / [30]	Radio frequency magnetron sputtering	To investigate the effect of the deposition temperature on the corrosion resistance and biocompatibility of the hydroxyapatite coatings	(i) base pressure = $1.3 \times 10^{-4}$ Pa; (ii) Argon working pressure = $6.6 \times 10^{-1}$ Pa; (iii) target power fed=50 W; (iv) substrate bias voltage=-60 V; (v) substrate temperature = 400°C, 500°C, 600°C, 700°C and 800°C; (vi) deposition time = 360 min; (vii) coatings thickness was about 450 nm.	(i) Crystalline content and the roughness of HA coatings increased with the deposition temperature; (ii) corrosion resistance of the thin film increase when substrate temperature increased to 700 °C; (iii) HA coatings deposited at 700–800 °C range has the best cell viability. (iv) Ca/P ratios of 1.67-1.81 range was revealed for all the coating samples as obtained from the EDS analysis; (v) XRD results showed increases in grain size and growth temperature due to the higher adatoms mobility resulting in crystallite aggregations.	(ii) Optimization should be done on the mechanism of corrosion degradation of the film and characterization of the tribological study will be interesting
HAP+Ti; Ti6Al4V / [31]	Radio-frequency (RF) magnetron sputtering	To investigate the mechanical properties and biocompatibility of the sputtered Ti-doped hydroxyapatite	(i) Pressure = $6.7 \times 10^{-1}$ Pa; (ii) deposition temperature = 700°C; (iii) deposition duration = 240 min; (iv) distance between target and substrate = 11 cm; (v) coating thickness= ~200 nm RF power target = (HA = 50 W); (TiO <sub>2</sub> = 0 W, 10 W, 17 W, and 25 W respectively)	(i) The AFM surface topography images result showed the coating roughness decreased with presence of Ti in the hydroxyapatite structure while mechanical and biological properties increases; (ii) Hardness and elastic modulus increased at the higher RF power [was power varied in the study?]; (iii) Enriching HA coating with Ti induces a good biocompatibility. (iv) The XPS analysis results showed the content of Ti increased with increase in the RF power feed on TiO <sub>2</sub> target	Appropriate addition of Ti into hydroxyapatite structure is needed for better biocompatibility and to improve the mechanical properties of Ti-6Al-4V substrate surfaces, so they could be used in biomedical as implants and bone substitutes.
HA/Ti; Ti-35Ta-xZr alloy / [32]	Radio-frequency and direct-current sputtering	To determine the surface characteristics of hydroxyapatite/titanium composite layer on the Ti-	(DC) Ti coating method = (i) Target Base pressure = $3.0 \times 10^{-5}$ Torr; (ii) Working pressure = $2.0 \times 10^{-2}$ Torr; (iii) Gas Ar <sub>2</sub> = 40 sccm; (iv) Pre-	(i) HA/Ti composite layer has better corrosion resistance compare to Ti layer as obtained via polarization behavior and impedance test; (ii) hydroxyapatite coating acts as the stable barrier in the increasing of the corrosion resistance; (iii) HA/Ti composite layer has a better	It would be interesting to study the tribological characteristics of the composite coatings

			35Ta-xZr surface by RF and DC sputtering	sputtering time = 20 min; (v) deposition time = 60 min; (vi) power =100 W. While, (RF) HA coating method = (i) Target base pressure = $3.0 \times 10^{-5}$ Torr; (ii) Working pressure = $2.0 \times 10^{-2}$ Torr; (iii) Gas Ar <sub>2</sub> = 40 sccm; (iv) Pre-sputtering = 20min; (v) deposition time =60 min; (vi) power =50 W	electrochemical behavior than the Ti single layer. (iv) XRD result revealed that the $\beta$ (211) peak emerged with the increased in Zr content;	
HA; Ti /[33]	Radio frequency (RF) magnetron sputtering	To investigate the (i) fabrication (ii) ultra-structure characterization (iii) in vitro studies of radio-frequency magnetron sputter deposited nano-hydroxyapatite coatings for biomedical applications	(i) Power =200 W; (ii) deposition time = 1 h, 2 hrs, and 3 hrs; (iii) pressure = 0.1 Pa; (iv) target-to-substrate distance = 40 mm; (v) Ti = (10 mm x 10 mm, 1 mm thick)	(i) Increase in the time lead to the increase in the coating thickness respectively; (ii) SEM image revealed CaP coating sputtered on acid-etched titanium surfaces over different deposition time showed the increased in thickness lead to increase in the average grain size (from $110 \pm 35$ to $360 \pm 120$ nm); (iii) The hydroxyapatite coatings deposited on acid-etched titanium was nanostructured low-crystallinity with thicknesses of 170, 250 and 440 nm via RF-magnetron sputtering; (iv) The uncoated Ti substrate has significantly lower degree of calcification in the fibrous collagen matrix; (v) The crystallite size increased from 40 to 46 nm with increased in the deposition time, indicating that the HA coating was nanocrystalline as obtained by Rietveld refinement.	Post deposition treatment needed to be done to improve the crystallinity of the coating and the adhesion	
HA; PTFE and Ti /[34]	Radio frequency (RF) magnetron sputtering	To investigate the RF magnetron sputtering of a hydroxyapatite target: a comparison study on polytetrafluorethylene and titanium substrates	(1) PTFE - (i) RF power = 300 W (ii) target diameter of 220 mm; (iii) deposition time = 2 hrs, 4 hrs, and 6 hrs; (2) Ti - (i) RF power = 500 W; (ii) deposition time = 2 hrs; (iii) Distance between target-substrate = 43 mm, (iv) base pressure = $10^{-4}$ Pa; (v) working pressure=0.4 Pa.	(i) XRD and XPS revealed the presents of Calcium fluoride and Calcium carbonate grown on Ti and PTFE samples surface; (ii) Hydroxyapatite coatings crystallinity and thickness increased with the increased in the deposition time; (iii) Phase-pure hydroxyapatite coating was not sputtered on the surface of PTFE and the technically Ti substrates; (iv) The microstructure of the coated Ti substrate showed no significant changes in different deposition runs compared to uncoated Ti while, the PTFE showed significant changes when sputtered compared to the uncoated PTFE.	Post deposition treatment, tribological study, and corrosion test should be carried out in the future study to aid better understanding of the thin film	
HA and Mg; Ti-	Radio-frequency (RF) magnetron	The used of X-ray absorption to study	(i) Base pressure = $2.7 \times 10^{-5}$ mbar; (ii) RF	(i) XRD result shows that the as-deposited film was amorphous while the annealed films showed	The effect of mechanical	

6Al-4V /[35]	sputtering	the local structure of Mg in hydroxyapatites thin films deposited by RF magnetron Co-Sputtering	power = 100 W; (iii) Sputtering pressure = $6.7 \times 10^{-3}$ mbar; (iv) time: HA target = 120 min, Mg target = 5 min; (v) distance between the target and substrate = 80 mm; (vi) Annealed = (temp = 1000 °C for 1 h with 5 °C/min heating rate)	the main peak is TiO <sub>2</sub> structure and a few secondary MgAl <sub>2</sub> O <sub>4</sub> ; (ii) Surface morphologies formed were highly agglomerated for the as-deposited while new agglomeration was formed on the annealed film due to the presence of TiO <sub>2</sub> ; (iii) EDX spectra of Ca, P, Mg, and O decreased during the annealing process as a result of temperature.	properties on the coating need to be carried out in the future study
HA; (AZ91) /[36]	Radio-frequency (RF) magnetron sputtering	To investigate the Bone marrow derived mesenchymal stem cell response to the RF magnetron sputter deposited hydroxyapatite coating on AZ91 magnesium alloy	(i) RF power = 400W; (ii) Ar atmosphere at 0.4Pa; (iii) deposition time = 600min; (iv) substrate pulse biasing = -25 V and -100V; duty cycle = 10%; (v) Substrate pre-treatment = (RF power=40 W; pulsed substrate bias -500V; Ar = 0.4Pa; t = 1h; Temp =300°C). (vi) heat treated at 400 °C for 2 hrs at heating rate of 1 °C/ min	(i) The HA-coated AZ91 data obtained from X ray diffraction showed that the studied samples consisted of the hexagonal HA phase (ii) EDS result showed that the Ca/P ratio magnitude for the coatings was in the same order (Ca/P=1.59–1.62); (iii) AFM images showed the microstructure of the HA coatings is grain-like; (iv) Negative bias voltage increased during deposition of hydroxyapatite effect the coating morphology, however, the phase composition and structure are the same. (v) There is surface cracking and micro holes formations as resulted from heat treatment.	The hydroxyapatite coating surface and nanoscale topography biological role should be taken into account and is required in future study
Si-HA; Si-Ti /[37]	Radio-frequency (RF) magnetron sputtering	To determine the structure of an RF-magnetron sputter-deposited silicate-containing hydroxyapatite-based coating investigated by high-resolution techniques	(i) RF power = 290 W; (ii) working pressure = 0.1 Pa; (iii) base pressure = $10^{-5}$ Pa; (iv) distance between target and substrate = 40mm; (v) deposition time = 1 h, 2 hrs, and 3 hrs; (vi) deposition temperature = RT to 200°C;	(i) The SEM result showed uniform coating at 3hrs and thickness of $790 \pm 50$ nm which corresponds to an average deposition rate of $4.4 \pm 0.3$ nm min <sup>-1</sup> ; (ii) Mobility of adatoms increased when ion bombardment and substrate temperature increases during deposition process ; (iii) Result obtained from EDX showed coating deposited at 3 hrs has higher Ca/P ratio 1.78l than HA stoichiometric (Ca/P=1.67); (iv) EDX result showed the coatings consists of Ca, P, O, and Si with Ca/P and Ca/(P+Si) ratios of 1.74 and 1.56, respectively; (v) XRD-analysis result showed the thin film was nanocrystalline with crystallite size of 10–50 nm range.	Appropriate optimization needs to be done in the future research on mechanical properties of the coating
HA; Ti-Ta-Zr /[38]	Magnetron-sputtering and electrochemical deposition	To investigate the Hydroxyapatite formation on biomedical Ti-Ta-Zr alloys by magnetron sputtering and electrochemical deposition	1) Electrochemical = (i) Counter electrode = Carbon; (ii) temperature = 80°C ± 1; (iii) Scan rate = 100 mV/s; (iv) No. cycles = 50; 2) RF sputtering = (i) Target = HA; (ii) Base pressure = 10–6 Torr; (iii)	(i) Optical microscopy result showed martensite microstructure with needle-like structures of Ti-25Ta-xZr and decreases with Zr content increases in Ti-25Ta-xZr system; (ii) The energy dispersive spectroscopy results showed Ti, Ta, Zr, Ca, and P. was presents in the coated layer; (iii) Radio frequency sputtering deposited a thicker plate-like precipitates than the hydroxyapatite plates deposited Ti-25Ta-xZr	The HA coating crystallinity is significant to lower the healing time after the clinical use of an implant. Therefore, heat treatment is needed for the proper controlled.



			Working pressure = $10^{-3}$ Torr; (iv) Gas Ar = (40 sccm); (v) Pre-sputtering time = 10min, (vi) Deposition time = 2hrs; (vii) supplied power = 45 W	alloys by electrochemical method; (iv) FE-SEM image result showed similar plate-like precipitates consisting of agglomerated hydroxyapatite particles for all morphologies of RF sputtered hydroxyapatite coatings on electrochemically HA-deposited Ti-25Ta-xZr alloys;	
Cap; Ti /[39]	Radio frequency magnetron sputtering	To investigate the radio frequency magnetron sputtering coatings deposited from biphasic calcium phosphate targets for biomedical implant applications	(i) RF power = 250 W; (ii) deposition time = 3 hrs; (iii) distance between target and substrate = 80 mm; (iv) working pressure = 0.7 Pa (v) Annealed in air = 700°C for 1 hr	(i) AFM images result revealed that the concentration of $\beta$ -Tricalcium phosphate in the biphasic targets increased leads to the formation of smaller surface features on the coatings' surfaces; (ii) XRD pattern after sputtering of the CaP coatings on the Ti result showed that the HA peak diffraction intensity was very weak due to the low coating's thickness; (iii) As-deposited coatings had high intensity peaks, attributed to the Ti substrate, while XRD patterns of CaP coatings after treatment showed peaks of TiO <sub>2</sub> (rutile) that appeared after annealing; (iv) The energy dispersive spectroscopy data result showed that an increased in the TCP content of biphasic targets leads to the deviation in the elemental composition of the films.	Characterization of mechanical properties and tribological study needed to be investigated in future study.

Overall, this overview showed that the properties of HA coating (microstructural, mechanical, and tribological properties) depend on the process parameters such as substrate condition, deposition parameters, and post-processing treatment. Hence, comprehensive research is still needed in the inquiry for optimizing design and process parameters. Biological role of the HA surfaces, nanoscale topography and exhaustive mechanical properties such as toughness of the coating should also be taken into account and is required in future study. However, more advanced characterizations such as X-ray photoelectron spectroscopy (XPS), topography, photoemission electron microscopy (PEEM) and transmission electron microscope (TEM) have been rarely reported.

### 3. Conclusions

The following conclusion can be deduced from the overview:

- (a) Sputtering is a good deposition technique for the deposition of HAP coating on the substrate due to its excellent adhesion and uniformity and ability to coat different surface geometry with minimal or no effect on the bulk properties.

(b) Several factors and parameters can affect the properties of the coatings, and make it increasingly difficult to directly compare the results of thin films coating from other sources. Factors such as the target and substrate condition, process parameters and the equipment used can all lead to large changes in the properties of the coating.

## Reference

- [1] S. R. Paital and N. B. Dahotre, "Calcium phosphate coatings for bio-implant applications: Materials, performance factors, and methodologies," *Mater. Sci. Eng. R Reports*, vol. 66, no. 1–3, pp. 1–70, Aug. 2009, doi: 10.1016/j.mserr.2009.05.001.
- [2] S. Bhat and A. Kumar, "Biomaterials and bioengineering tomorrow's healthcare," *Biomatter*, vol. 3, no. 3, p. e24717, Jul. 2013, doi: 10.4161/biom.24717.
- [3] G. Singh, K. Agrawal, S. Singh, and S. Prakash, "Hydroxyapatite coating for bio implants and problem associated with coating techniques: a review," no. December, pp. 250–255, 2010.
- [4] S. R. Paital and N. B. Dahotre, "Calcium phosphate coatings for bio-implant applications: Materials, performance factors, and methodologies," *Mater. Sci. Eng. R Reports*, vol. 66, no. 1–3, pp. 1–70, Aug. 2009, doi: 10.1016/j.mserr.2009.05.001.
- [5] M. F. Morks and A. Kobayashi, "Effect of gun current on the microstructure and crystallinity of plasma sprayed hydroxyapatite coatings," *Appl. Surf. Sci.*, vol. 253, no. 17, pp. 7136–7142, Jun. 2007, doi: 10.1016/j.apsusc.2007.02.183.
- [6] I. V. Pylypchuk, A. L. Petranovskaya, P. P. Gorbyk, A. M. Korduban, P. E. Markovsky, and O. M. Ivasishin, "Biomimetic Hydroxyapatite Growth on Functionalized Surfaces of Ti-6Al-4V and Ti-Zr-Nb Alloys," *Nanoscale Res. Lett.*, 2015, doi: 10.1186/s11671-015-1017-x.
- [7] K. Mediaswanti, C. Wen, E. P., C. C. Berndt, and J. Wang, "Sputtered Hydroxyapatite Nanocoatings on Novel Titanium Alloys for Biomedical Applications," in *Titanium Alloys - Advances in Properties Control*, InTech, 2013.
- [8] V. Nguyen, T. Cheng, T. Fang, and M. Li, "The fabrication and characteristics of hydroxyapatite film grown on titanium alloy Ti-6Al-4V by anodic treatment," *J. Mater. Res. Technol.*, no. x x, Mar. 2020, doi: 10.1016/j.jmrt.2020.03.002.
- [9] N. Kantharia, S. Naik, S. Apte, M. Kheur, S. Kheur, and B. Kale, "Review Article Nano - hydroxyapatite and its contemporary applications Results of Restorative Applications of nHA Fillers in restorative GICs," *JDRSD*, vol. 1, no. 1, pp. 15–9, 2014.
- [10] D. S. Gomes, A. M. C. Santos, G. A. Neves, and R. R. Menezes, "A brief review on hydroxyapatite production and use in biomedicine," *Cerâmica*, vol. 65, no. 374, pp. 282–302, Jun. 2019, doi: 10.1590/0366-69132019653742706.
- [11] J. Weng, "Formation and characteristics of the apatite layer on plasma-sprayed hydroxyapatite coatings in simulated body fluid," *Biomaterials*, vol. 18, no. 15, pp. 1027–1035, Aug. 1997, doi: 10.1016/S0142-9612(97)00022-7.

- [12] P. Cheang and K. A. Khor, "Thermal spraying of hydroxyapatite (HA) coatings: Effects of powder feedstock," *J. Mater. Process. Technol.*, vol. 48, no. 1–4, pp. 429–436, Jan. 1995, doi: 10.1016/0924-0136(94)01679-U.
- [13] P. Rajesh, C. V. Muraleedharan, M. Komath, and H. Varma, "Pulsed laser deposition of hydroxyapatite on titanium substrate with titania interlayer," *J. Mater. Sci. Mater. Med.*, vol. 22, no. 3, pp. 497–505, Mar. 2011, doi: 10.1007/s10856-011-4230-x.
- [14] M. Khalid, M. Mujahid, A. N. Khan, and R. S. Rawat, "Dip Coating of Nano Hydroxyapatite on Titanium Alloy with Plasma Assisted  $\gamma$ -Alumina Buffer Layer: A Novel Coating Approach," *J. Mater. Sci. Technol.*, vol. 29, no. 6, pp. 557–564, Jun. 2013, doi: 10.1016/j.jmst.2013.02.003.
- [15] E. Ertürk, M. Dalkiz, E. Özyilmaz, H. Z. Akbaş, H. Ali Çetinkara, and H. Aykul, "The evaluation of the effects of surface treatments on different dental ceramic structures," *J. Biomech.*, vol. 44, no. 5, p. 13, May 2011, doi: 10.1016/j.jbiomech.2011.02.050.
- [16] M. Yoshinari, Y. Ohtsuka, and T. Derand, "Thin hydroxyapatite coating produced by the ion beam dynamic mixing method," *Biomaterials*, vol. 15, no. 7, pp. 529–535, Jun. 1994, doi: 10.1016/0142-9612(94)90019-1.
- [17] K. Grandfield and I. Zhitomirsky, "Electrophoretic deposition of composite hydroxyapatite–silica–chitosan coatings," *Mater. Charact.*, vol. 59, no. 1, pp. 61–67, Jan. 2008, doi: 10.1016/j.matchar.2006.10.016.
- [18] E. Mohseni, E. Zalnezhad, and A. R. Bushroa, "Comparative investigation on the adhesion of hydroxyapatite coating on Ti–6Al–4V implant: A review paper," *Int. J. Adhes. Adhes.*, vol. 48, pp. 238–257, Jan. 2014, doi: 10.1016/j.ijadhadh.2013.09.030.
- [19] R. Surmenev, A. Vladescu, M. Surmeneva, A. Ivanova, M. Braic, I. Grubova and C. M. Cotrut, "Radio Frequency Magnetron Sputter Deposition as a Tool for Surface Modification of Medical Implants," in *Modern Technologies for Creating the Thin-film Systems and Coatings*, InTech, 2017.
- [20] A. Vladescu, I. Birlik, V. Braic, M. Toparli, E. Celik, and F. Ak Azem, "Enhancement of the mechanical properties of hydroxyapatite by SiC addition," *J. Mech. Behav. Biomed. Mater.*, vol. 40, pp. 362–368, Dec. 2014, doi: 10.1016/j.jmbbm.2014.08.025.
- [21] O. Oluwatosin Abegunde, E. Titilayo Akinlabi, O. Philip Oladijo, S. Akinlabi, and A. Uchenna Ude, "Overview of thin film deposition techniques," *AIMS Mater. Sci.*, vol. 6, no. 2, pp. 174–199, 2019, doi: 10.3934/matserci.2019.2.174.
- [22] M. Amorim, R. Savio, H. Santiago, and M. Massi, "Recent Developments on Silicon Carbide Thin Films for Piezoresistive Sensors Applications," in *Silicon Carbide - Materials, Processing and Applications in Electronic Devices*, no. June 2014, InTech, 2011.
- [23] P. Silva-Bermudez, G. Ramirez, and S. E. Rodil, "Corrosion resistant coatings for dental implants," in *Bio-Tribocorrosion in Biomaterials and Medical Implants*, Elsevier, 2013, pp. 250–308.
- [24] F. M. Mwema, O. P. Oladijo, S. A. Akinlabi, and E. T. Akinlabi, "Properties of physically deposited thin aluminium film coatings: A review," *J. Alloys Compd.*, vol. 747, pp. 306–323, May 2018, doi: 10.1016/j.jallcom.2018.03.006.
- [25] J. A. Lenis, M. A. Gómez, and F. J. Bolívar, "Effect of deposition temperature and target-substrate distance on the structure, phases, mechanical and tribological properties of multi-layer HA-Ag coatings obtained by RF magnetron sputtering," *Surf. Coatings Technol.*, vol. 378, no. June, p. 124936, 2019, doi: 10.1016/j.surfcoat.2019.124936.

- [26] A. Das, A. K. Chikkala, G. P. Bharti, R. R. Behera, R. S. Mamilla, A. Khare, and P. Dobbidi, "Effect of thickness on optical and microwave dielectric properties of Hydroxyapatite films deposited by RF magnetron sputtering," *J. Alloys Compd.*, vol. 739, pp. 729–736, Mar. 2018, doi: 10.1016/j.jallcom.2017.12.293.
- [27] D. Kong, D. Long, Y. Wu, and C. Zhou, "Mechanical properties of hydroxyapatite-zirconia coatings prepared by magnetron sputtering," *Trans. Nonferrous Met. Soc. China*, vol. 22, no. 1, pp. 104–110, Jan. 2012, doi: 10.1016/S1003-6326(11)61147-3.
- [28] J. A. Lenis, F. M. Hurtado, M. A. Gómez, and F. J. Bolívar, "Effect of thermal treatment on structure, phase and mechanical properties of hydroxyapatite thin films grown by RF magnetron sputtering," *Thin Solid Films*, vol. 669, no. November 2018, pp. 571–578, Jan. 2019, doi: 10.1016/j.tsf.2018.11.045.
- [29] M. A. Surmeneva, T. M. Mukhametkaliyev, A. I. Tyurin, A. D. Teresov, N. N. Kovalc, T. S. Pirozhkova, I. A. Shuvarin, A.V. Shuklinov, A.O. Zhigachev, C. Oehr, and R. A. Surmenev, "Effect of silicate doping on the structure and mechanical properties of thin nanostructured RF magnetron sputter-deposited hydroxyapatite films," *Surf. Coatings Technol.*, vol. 275, pp. 176–184, Aug. 2015, doi: 10.1016/j.surfcoat.2015.05.021.
- [30] A. Vladescua, M. Braic, F. Ak Azem, I. Titorencu, V. Braica, V. Prunac, A. Kissa, A.C. Parau, and I. Birlik, "Effect of the deposition temperature on corrosion resistance and biocompatibility of the hydroxyapatite coatings," *Appl. Surf. Sci.*, vol. 354, pp. 373–379, Nov. 2015, doi: 10.1016/j.apsusc.2015.05.059.
- [31] A. Vladescu, S.C. Padmanabhan, F. A. Azem, M. Braic, I. Titorencu, I. Birlik, M. A. Morris, and V. Braic, "Mechanical properties and biocompatibility of the sputtered Ti doped hydroxyapatite," *J. Mech. Behav. Biomed. Mater.*, vol. 63, pp. 314–325, Oct. 2016, doi: 10.1016/j.jmbbm.2016.06.025.
- [32] W.-G. Kim and H.-C. Choe, "Surface characteristics of hydroxyapatite/titanium composite layer on the Ti-35Ta-xZr surface by RF and DC sputtering," *Thin Solid Films*, vol. 519, no. 20, pp. 7045–7049, Aug. 2011, doi: 10.1016/j.tsf.2011.04.090.
- [33] M. A. Surmeneva, R. A. Surmenev, Y. A. Nikonova, I. I. Selezneva, A. A. Ivanova, V. I. Putlyaev, O. Prymak, and M. Epple, "Fabrication, ultra-structure characterization and in vitro studies of RF magnetron sputter deposited nano-hydroxyapatite thin films for biomedical applications," *Appl. Surf. Sci.*, vol. 317, pp. 172–180, Oct. 2014, doi: 10.1016/j.apsusc.2014.08.104.
- [34] R. A. Surmenev, M. Surmeneva, I. Grubova, R. Chernozem, B. Krause, T. Baumbach, K. Loza, and M. Epple, "RF magnetron sputtering of a hydroxyapatite target: A comparison study on polytetrafluorethylene and titanium substrates," *Appl. Surf. Sci.*, vol. 414, pp. 335–344, Aug. 2017, doi: 10.1016/j.apsusc.2017.04.090.
- [35] A. Bootchanont, T. Wechprasit, M. Horprathum, C. Chananonawathorn, P. Amonpattaratkit, W. Klysubun, R. Yimnirun, Atchara Khamkongkaeo, N. Barnthip, and W. Sailuam, "X-ray absorption study of the local structure of Mg in hydroxyapatites thin films deposited by RF magnetron Co-Sputtering," *Radiat. Phys. Chem.*, vol. 172, no. February, p. 108788, Jul. 2020, doi: 10.1016/j.radphyschem.2020.108788.
- [36] M. A. Surmeneva, A. A. Ivanova, Q. Tian, R. Pittman, W. Jiang, J. Lin, H. H. Liu, and R. A. Surmenev, "Bone marrow derived mesenchymal stem cell response to the RF magnetron sputter deposited hydroxyapatite coating on AZ91 magnesium alloy," *Mater. Chem. Phys.*, vol. 221, no. October 2017, pp. 89–98, Jan. 2019, doi: 10.1016/j.matchemphys.2018.09.030.

- [37] M. A. Surmeneva, M. V. Chaikina, V. I. Zaikovskiy, V. F. Pichugin, V. Buck, O. Prymak, M. Epple, and R. A. Surmenev, "The structure of an RF-magnetron sputter-deposited silicate-containing hydroxyapatite-based coating investigated by high-resolution techniques," *Surf. Coatings Technol.*, vol. 218, no. 1, pp. 39–46, Mar. 2013, doi: 10.1016/j.surfcoat.2012.12.023.
- [38] H.-J. Kim, Y.-H. Jeong, H.-C. Choe, and W. A. Brantley, "Hydroxyapatite formation on biomedical Ti–Ta–Zr alloys by magnetron sputtering and electrochemical deposition," *Thin Solid Films*, vol. 572, pp. 119–125, Dec. 2014, doi: 10.1016/j.tsf.2014.07.058.
- [39] K. A. Prosolov, K. S. Popova, O. A. Belyavskaya, J. V. Rau, K.A. Gross, A. Ubelis, and Y.P. Sharkeev, "RF magnetron-sputtered coatings deposited from biphasic calcium phosphate targets for biomedical implant applications," *Bioact. Mater.*, vol. 2, no. 3, pp. 170–176, Sep. 2017, doi: 10.1016/j.bioactmat.2017.07.003.