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Hybrid Nanocomposites Produced by Sputtering: Interaction with Eukaryotic and Prokaryotic Cells

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Additional information is available at the end of the chapter

Abstract

The use of composite materials for different and diverse technological applications is a growing field. The development of this class of materials arises when it is required from a material a combination of properties that are impossible to co-exist, such as, for example, high hardness and good tenacity. However, in some applications the main focus of this combination of characteristics/properties is only required at the material surface; in this cases, the composite will be deposited onto the surface as a coating. Moreover, the introduction of reinforcements of nanometric size, where one of the dimensions is lower than 100 nm, may induce, in the deposited composite, particularly appealing properties due to the nanometric scale. This chapter presents the use of a particular deposition technique—sputtering—for the production of nanocomposites made of dissimilar materials such as ceramic/metal, ceramic/polymer and ceramic/polymer/metal. The application of these surfaces in interaction with both eukaryotic and prokaryotic cells will be given as an example of the broad range of applications of the developed surfaces.

Keywords: hybrid nanocomposites, sputtering, dissimilar materials, thin films, prokaryotic and eukaryotic cells

1. Introduction

In this introduction, a brief overview of the sputtering process is given based on a working class manuscript [1], but excellent reviews on the process have been published (see, e.g., Ref. [2]).

Sputtering is one of the techniques of coating a material by physical vapor deposition (PVD). Sputtering consists in the ejection of particles, atoms or clusters, by the bombardment of a solid or target by energetic particles, mostly ions. It results from collisions between the

incident energetic particles, and/or resultant recoil atoms, with surface atoms. A measure of the removal rate of surface atoms is the sputter yield Y, defined as the ratio between the number of sputter ejected species and the number of incident particles. Sputtering only occurs if the incident particles have enough energy to overcome the binding energy of the elements that constitute the material. In a deposition chamber under reduced pressure, a discharge is established between the cathode (target material from where the particles are ejected) and the anode (substrate onto which the coating will be formed). Usually there are three distinct phases in the sputtering process: (i) ejection of the target material; (ii) transport of the ejected material and (iii) nucleation and growth of the film. The control of several deposition parameters in each one of these three phases allow to a perfect control over the deposited thin film and obtaining tailor made materials, which are not predicted by conventional thermodynamics.

The ejection of the target material is achieved by simply momentum transfer between the ionic rare gas positive ions with the constituent material of the target. Argon is one of the most commonly used rare gases. It is an inert gas and therefore has the advantage of not change the chemistry of the target material by reacting with the ejected species. It has an atomic weight that guarantees the adequate sputtering of most of the chemical elements, has a low cost and high availability in the market, and can be purchased with high purity. In the course of the ionization inside the chamber, a plasma is formed which needs to be stable, in order for the process to proceed. In order to induce the plasma positive ions collision with the target, they must be accelerated by a negative potential. For this reason, the applied deposition power must be high, so that the ions can acquire sufficient energy to promote the ejection of secondary electrons from the target, contributing to the maintenance of plasma. The pressure in the deposition chamber needs to be well-controlled in order to promote a high number of collisions between the secondary electrons and the gas atoms, allowing ionization to proceed and ensure the maintenance of the plasma. However, it must not be too high, as in this case, argon ions will suffer too many collisions in their path, diminishing the free mean path, leading to loss of energy and arriving at the target with lower energy that the one needed to promote sputtering.

If they have enough energy, the ejected particles from the target are transported through the plasma to the substrate, where they eventually deposit and form the coating. The trajectory of the ejected particles is random, in their direction, following a cosine law. The process of the formation of the coating can also be considered in three phases (**Figure 1**). In the first phase, the atoms ejected from the target transfer their kinetic energy to the substrate, becoming "adatoms," that is, nonbonded atoms. In the second phase, the adatoms diffuse superficially over the substrate where they either suffer desorption or are accommodated in a low surface energy location onto the substrate. Finally, the third phase takes place when the atoms readjust their position in the network by bulk diffusion processes.

The properties of the films deposited by this technique depend on the material of the target, the gas used for the discharge and deposition parameters such as pressure, target-distance, polarization of the substrate and the chemical composition of the discharge gas. In fact, in addition to the nonreactive noble gas, the discharge gas, others can be added such as oxygen, nitrogen or methane. In these cases, the sputtering is said to occur in a reactive mode. The use of a magnetron associated with the cathode creates a magnetic field that imposes compulsory trajectories to the electrons ejected by the target, increasing the bombardment density.
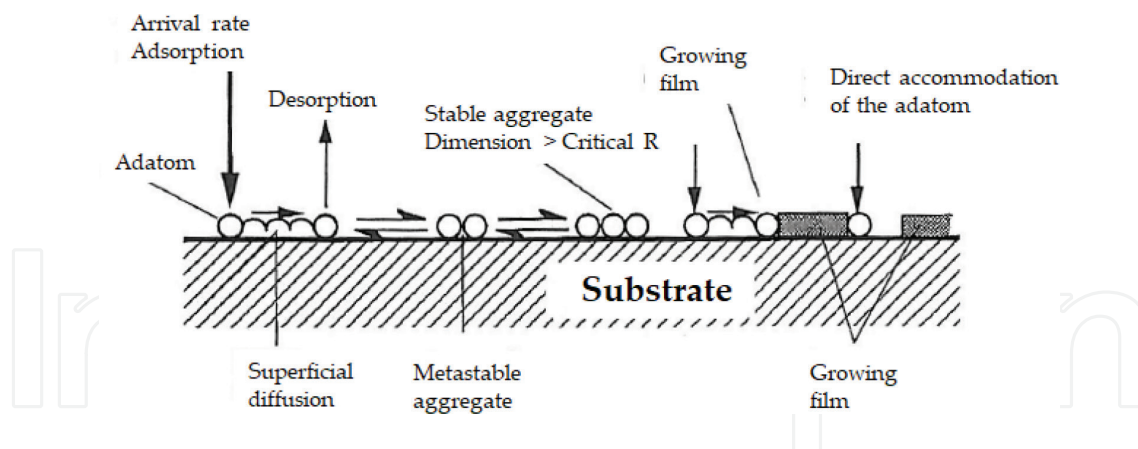
Figure 1. Schematic representation of the nucleation and grow of a film deposited by sputtering.

2. Production of nanocomposites

The use of composites is usually required when the materials or its surface must present a combination of properties/characteristics that are not possible to obtain from a single material. The materials for the matrix can be either organic, polymeric materials, or inorganic, such as ceramics and metals or metal alloys. In addition, the fillers can belong to these two classes of materials. When one of the dimensions of the filler is of nanometric scale, lower than 100 nm, it is called nanofiller and the resulting material a nanocomposite. The most commonly used inorganic nanofillers are carbides, nitrides, borides, oxides, metallic particles, clay, carbon nanotubes, nanodiamond and, more recently, graphene. Regarding the organic nanofillers, the most common, depending on the application, are polytetrafluoroethylene, nanocellulose fibers or cellulose nanocrystals. Nevertheless, some combinations of matrix and reinforcement are not able to be produced by conventional methods. In fact, the reinforcement of a metallic matrix with an organic nanofiller is forbidden, as the processing temperature of the metal material occurs at a temperature that completely degrades the organic filler. There are an extensive number of excellent reviews on the production of nanocomposites (see Refs. [3, 4] as examples) and some brief examples, based in these two references, are given.

The sol–gel method is suitable for obtaining nanocomposites coatings with a thickness up to 1 μm. However, the method presents several drawbacks, namely its application onto metallic substrates, crackability and not appropriate if a thermal treatment is required. This method can be used in combination with sputtering or electrodeposition.

Chemical vapor deposition (CVD) method is usually used for the fabrication of inorganic/inorganic nanocomposites coatings and, sometimes, in order to improve the quality of the coatings, the aerosol-assisted CVD can be used. Some organic (matrix)/inorganic nanocomposites have also been produced by this method.

Physical vapor deposition (PVD) technology includes evaporation and sputtering, among other less used technologies. It can be used for the production of hybrid nanocomposites and, especially sputtering, as described in the next point of this chapter, is one of the most versatile for the production of a great combination of inorganic/organic nanocomposites.

The thermal spray method is often used for making nanocomposites with a metallic matrix. The spray material is a nanosized metallic or alloyed powder that is dispersed into a solution in order to conduct plasma thermal spraying.

Electroless deposition method is often used for producing nanocomposite coatings with polymeric matrix where the nanofillers are carbides, nitrides, borides or other polymers. In order to improve the mechanical and degradation properties of the coatings, a thermal treatment is made.

Electrodeposition method is used for the production of nanocomposites which contain organic nanofillers dispersed in organic or inorganic matrix. By changing the duty cycle and frequency during pulsed electrodeposition can also produce nanocomposite coatings.

Spray coating and spin coating methods are widely used for the preparation of polymeric-based nanocomposites. However, the latter can only be used for coating flat substrates and, therefore, is mostly used for the preparation of thin-film nanocomposite coatings.

Dip coating is a method widely used in the industry. It consists of soaking the substrate in a solution with the nanocomposite and pulled up at a constant and controlled speed. Some of the advantages of this method are that the solution can be reused until evaporation or depletion. The disadvantages are mainly related with the poor adhesion between the substrate and the coating, which makes this method unsuitable for a number of applications.

3. Application of sputtered hybrid nanocomposites

3.1. Interaction with eukaryotic cells

With the advance of technology and medical research, the replacement of hard tissues is essential for improving the quality of life of an aging population. Implants placed in contact with biological tissues should promote a positive response; they must be bioactive and biocompatible. For orthopedic and orthodontic applications, hydroxyapatite (HA) is the gold standard due to its chemical mimicking of the inorganic constitution of human hard tissue [5]. The use of HA as a coating is justified when the economic factor imposes and cheaper bulk materials, such as 316L stainless steel, are used to replace the much more expensive commercial pure titanium (Ti cp) or titanium alloys.

The use of HA-based nanocomposites has been described in the literature. One of the elements used to dope HA coatings is yttrium (Y) which is a transition metal with hydrophilic characteristics [6], used to improve the mechanical properties of ceramic materials [7] and, when bonded to hydroxyapatite, lowers its electrical resistance. When yttrium reinforced hydroxyapatite was used as a coating, it was found to possess a greater ability to form apatite when in contact with biological fluids than the HA coating [8].

Magnesium (Mg) is an element that is involved in the early mineralization process and is necessary to ensure adequate function of osteoblasts and osteoclasts. For this reason, studies are also reported in the literature in which HA coatings are doped with this element. The effect of the incorporation of magnesium in HA on the adhesion of osteoblasts showed that cell adhesion

was higher in the co-deposited samples compared to the control samples without Mg [9]. Another element that is known to cause the increase of the number of osteoblasts and reduce the activity of osteoclasts is strontium (Sr). This is the reason why it is recommended in several countries as treatment of osteoporosis [10]. Its integration into hydroxyapatite coatings demonstrated a 46% increase in the area of contact between bone and implant when compared to the HA monolithic coatings [11]. This study also demonstrated that the osteoconductivity of doped coatings was not only faster but also provided a better quality of bone-implant integration.

Moreover, other metallic elements such as cobalt (Co), chromium (Cr) and nickel (Ni) were used in hydroxyapatite composites [12] to study their effect on the *in vitro* growth of an apatite layer. This study demonstrated that metal ions can be incorporated during the mineralization process affecting its structure and size and, consequently, the quality of the mineral coating.

Also, all ceramic composites, such as those obtained from the incorporation of ZrO_2 into HA, decreased the porosity and surface area of the coating and inhibited the proliferation of microorganisms, implying their possible use as biomaterials that may reduce the inflammatory process, according to a published study [13]. The same type of nanocomposites was also obtained by adding TiO_2 (10 wt%) to HA to determine the potential of the composite in the development, adhesion and growth of mesenchymal cells, as well as their ability to differentiate into osteoblasts. The results indicated that TiO_2-HA coatings were structurally nanocomposites with highly osteoinductive capacity, allowing their possible use as coatings for implants that support high loads. Moreover, also doping HA films with magnesium oxide (MgO) allowed to obtain better corrosion resistance and lower porosity of the coatings both when in contact with simulated human fluids and under conditions of osteoclastic resorption *in vivo* [14].

Silicon (Si) is a chemical element that is found in active zones of calcification. Its absence is associated with a poor production of collagen that reduces bone proliferation leading to the appearance of deformations and lesions. For this reason, it is a very important chemical element in the early stages of bone mineralization and soft tissue development [15]. Some of the invoked benefits are related to the release of small amounts of silicon ions, which stimulate the activity of seven families of genes, increasing osteoblasts proliferation and differentiation. In addition, silicon increases the solubility of the coatings by generating a more electronegative surface resulting in a surface biologically equivalent to apatite [16]. The development, in our laboratory, of hybrid sputtered nanocomposite HA/Si coatings confirmed these claims and the results presented here have never been published before.

The coatings were deposited, onto 316L stainless steel, by sputtering r.f. magnetron from HA target doped with silicon foils. The choice of steel is related to economic factors (especially in the context of economic crisis) given the price of the materials used in this type of implant—titanium and its alloys. The use of 2 and 4 10 × 10 mm Si foils gave rise to coatings with atomic percentages of Si of 2 (HA/Si2) and 4 (HA/Si4), respectively.

The thin films, with thickness of approximately 700 nm, demonstrated a nanocomposite structure (**Figure 2**) with an average surface roughness (Sa) of 15 , 63 and 29 nm for HA, HA/Si2 and HA/Si4, respectively. All the surfaces presented moderate overall hydrophilic characteristics, although the surfaces of HA doped with elemental Si reveal a heterogeneous distribution of
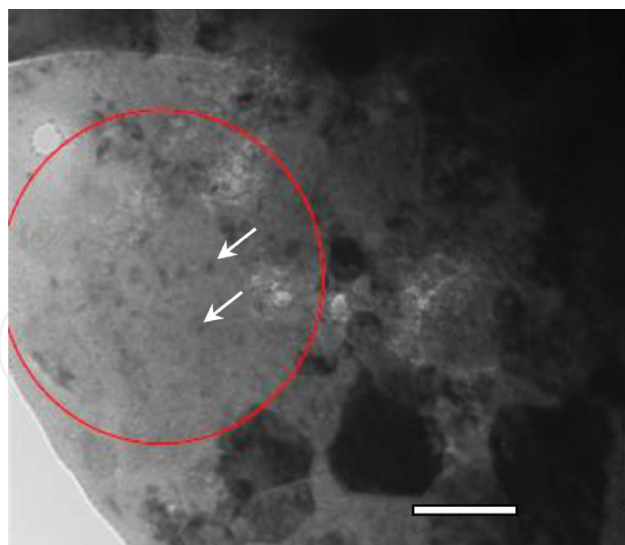
Figure 2. TEM bright field image of HA4 sample, highlighting the heterogeneous distribution (circle) of the nanosized Si (arrows); bar = 100 nm.

hydrophobic domains, as determined by dynamic contact angles studies (**Figure 3**). This can be related with the heterogeneous distribution of Si onto the HA matrix as reveled by the bright field TEM micrograph. In fact, the addition of Si changes the behavior of the monolithic HA coating. For surface HA2, it is apparent that the forward angle is not constant revealing the existence of heterogeneously hydrophobic domains distributed on the surface, which also influence the value of the contact angle during the retraction step. When the content of the reinforcement element increases, HA4, this behavior is more evident since the presence of the hydrophobic domains prevents the free spreading of the water causing the contact angle to increase from 40° to about 140°. When the volume of water is high enough to overcome this barrier, the liquid spreads freely reaching a value that remains constant during the step of decreasing the volume of liquid.

For biomedical applications, a surface charge value, given by the zeta potential (ζ), between −30 and 30 mV is considered unstable. Therefore, it is required that the potential value of the surfaces stays outside this range. Also, the pH value is a factor that influences the value of the zeta potential. In fact, the physiological pH comprises the minimum values of 6.8 (denominated acidosis) to a maximum limit of 8.0 (denominated alkalosis), being its normal value 7.4. The evaluation of zeta potential, in a KCl 1 mM solution, between pH values of 3 and 10 showed that the produced monolithic and nanocomposites thin films present stable zeta potential values, for the range of biological pH values. Moreover, for the physiological pH value all the sputtered surfaces have lower zeta potential values than the 316L substrate (−35.8 mV), determined with the same electrolyte. Published studies [17] show that a more negative zeta potential value implies a better adsorption of the extracellular matrix and increases binding of fibroblasts. It should be highlighted the higher standard deviation observed in the determination of the zeta potential values of sample HA 4 (−80 ± 30 mV), which indicates that the surface is reacting with the electrolyte. This observation is valuable for the envisaged application, where the dissolution of the coating with the consequent deposition of an apatite like layer is mandatory for a good osteoinductive coating.
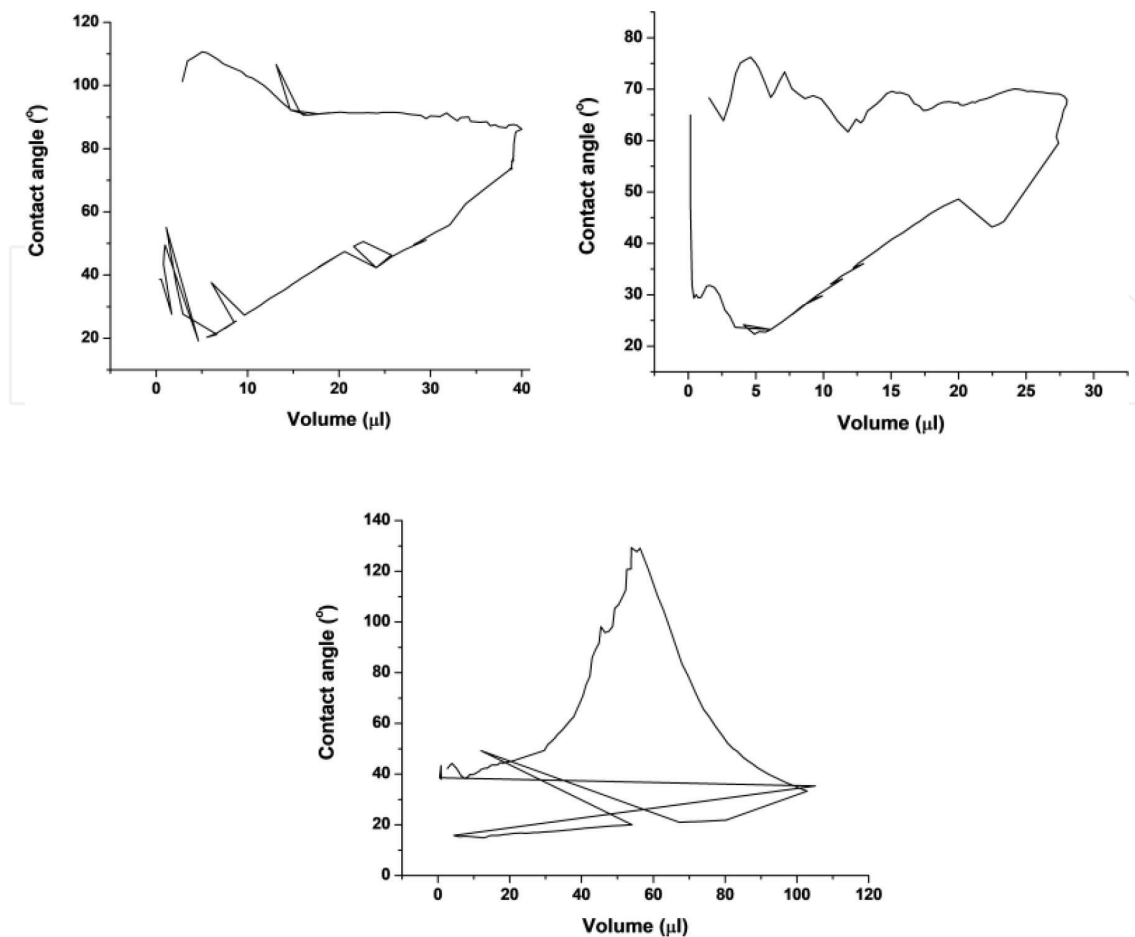
Figure 3. Dynamic contact angle characterization of surfaces (a) HA, (b) HA2 and (c) HA4.

When preliminary *in vitro* tests were made, by 14 days immersion in Hanks balanced salt solution (HBSS), at 37°C, under shaking conditions (100 rpm), the formation of an apatite like layer was more exuberant in the HA4 coating due to the more rapid dissolution of the Si ions as expected from the previous results (**Figure 4**).

All the previous characterization indicated that the hybrid nanocomposite HA4 could induce a better interface for the adhesion and proliferation of osteoblastic cells. For this reason, all the films were tested with MG63 osteoblastic cells line. This biological system allows a homogenous and proliferative population that contains phenotypic characteristics of normal osteoblastic cells, including hormonal response and genetic expression, and is frequently used as an osteoblast model for *in vitro* studies. The confocal laser microscopy images (**Figure 5**) show that MG63 cells adhere to all surfaces, as can be seen in the images corresponding to day 1.

The HA film shows cells with rounded morphology and also with elongated morphology. Comparatively, cell adhesion and cytoplasmic growth are more pronounced in the films HA2 and HA4, where the cells have a typical elongated morphology, expected for 24 h cultures and greater cytoplasmic expansion. After 5 days, the MG63 cells proliferated on the surfaces which are partially covered by an organized cell layer. The images suggest that the proliferation is more abundant in the HA2 and HA4 surfaces when compared to the HA surface. In the latter
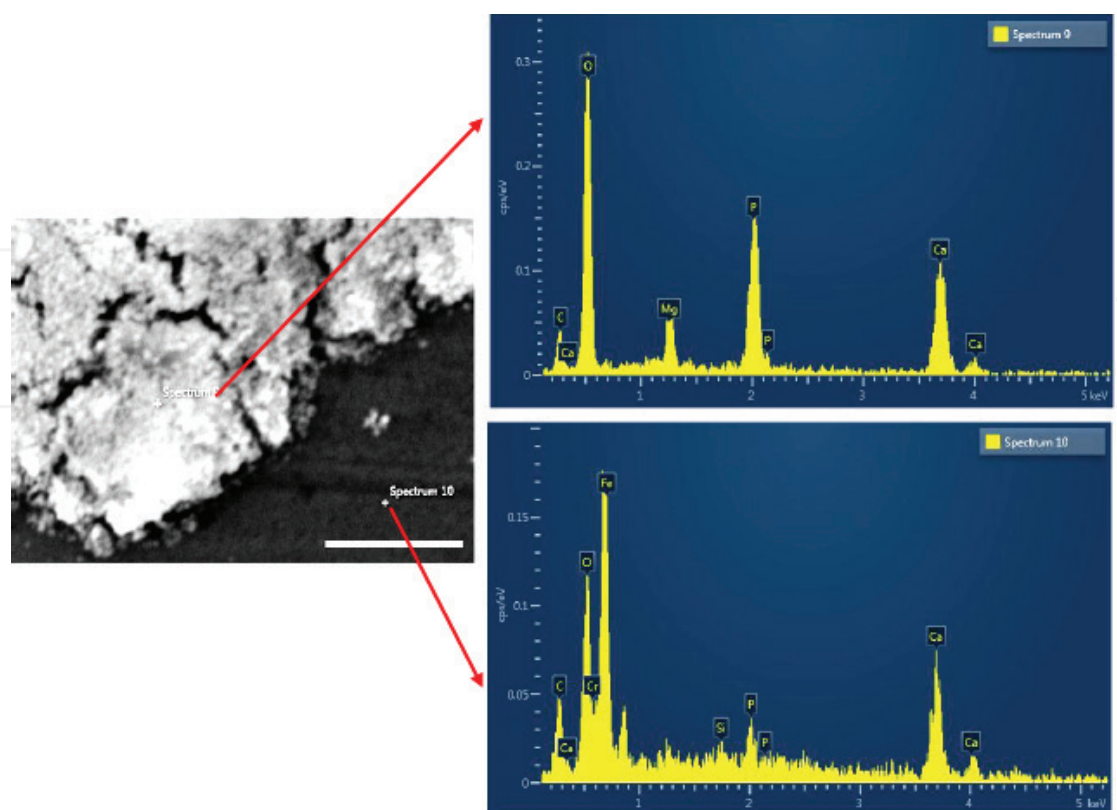
Figure 4. Scanning electron microscopy micrograph of the HA4 after 14 days in Hanks solution. The energy disperse spectra show that the formed layer is composed of the same chemical elements as apatite.

occurred an abnormal proliferation of cellular clusters in which cell division occurred, but not a normal cytoplasmic expansion, presenting an altered F-actin cytoskeleton. In comparison, HA2 and HA4 nanocomposite surfaces exhibit an organized cell layer with elongated/polygonal morphology, normal organization of the cytoskeleton F-actin (with greater staining intensity at the cell boundaries) and perfect contact between cells.

In summary, the addition of silicon to hydroxyapatite, in the form of hybrid nanocomposite thin films, induces a set of properties/characteristics that are ideal for promoting cell adhesion and proliferation: controlled structural order, good wettability, concordant surface charge, nanometer scale size and surface nanotopography.

3.2. Interaction with prokaryotic cells

In order to give a different perspective of the same problem, the prevention of bacterial infection in orthopedic implants will be presented. Especial relevance will be given to hydroxyapatite (HA) coatings doped with two known antibacterial elements: silver (Ag) and fluorine (F).

Over the past decades, several studies have been made concerning the antibacterial effect of HA-Ag coatings in order to evaluate their efficiency [18–21]. Despite some contradictory results, it is generally accepted that silver can contribute for the antibacterial effect although the mechanisms responsible for this action is far from being completely understood [22]. It also known that the nanometric size of the silver particles in the composite is responsible
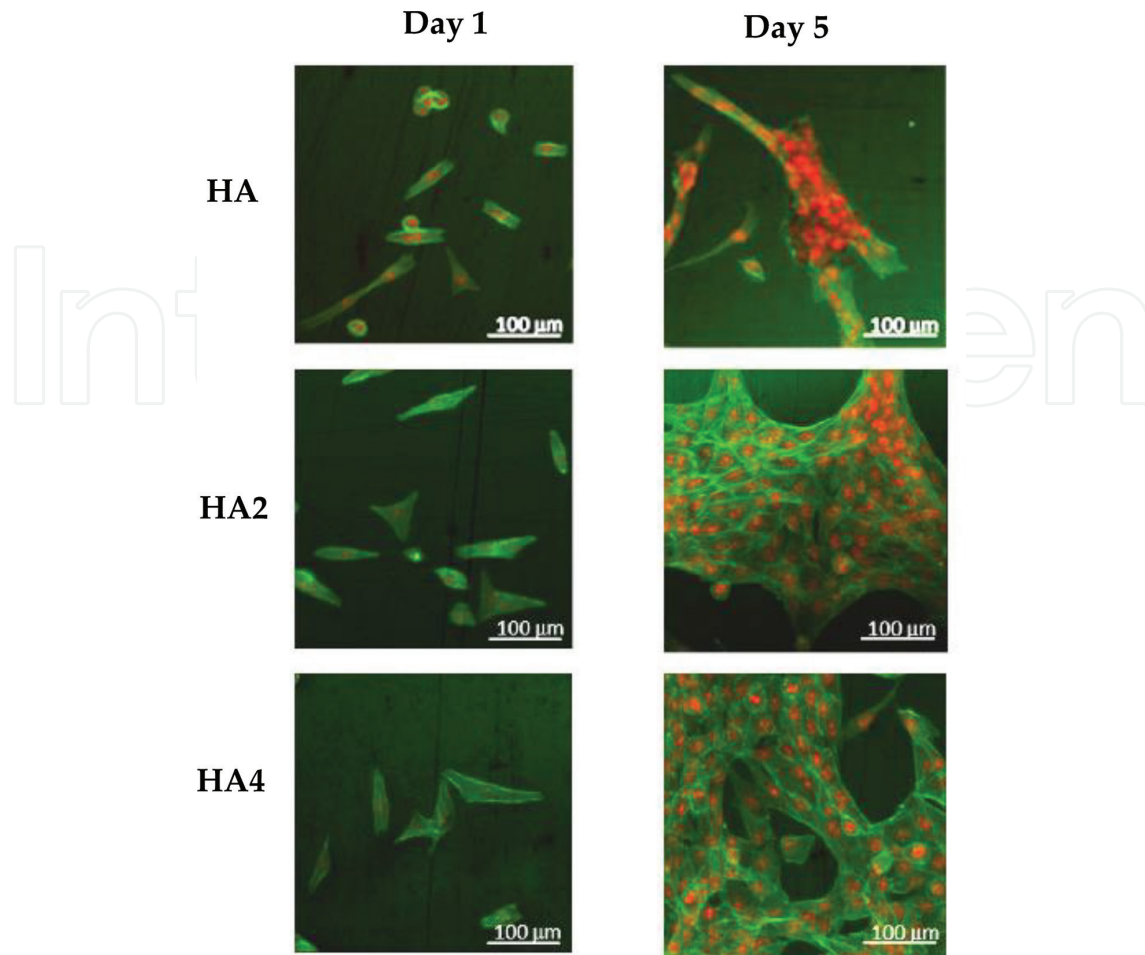
Day 1   **Day 5**

Figure 5. Confocal laser microscopy images of the nanocomposites after 1 and 5 days of culture with MG63 cells (red = nucleus; green = F actin from cytoskeleton).

for a more efficient effect [23] due to the more rapid kinetic of silver ions production, when compared with micrometric size silver.

Concerning the effects of fluorine, some of the studies done on HA coatings have focused on the incorporation of this element into the hydroxyapatite structure, $Ca_{10}(PO_4)_2F_x(OH)_{2-x}$, where the F^- ions replace the OH^- groups. The results show that by incorporating fluorine it is possible to improve the characteristics of hydroxyapatite [17]. HA with hydroxyl groups partially replaced by F has been the subject of some investigation due to the considerable presence of partially fluoridated HA in bones and teeth. Fluoride promotes the mineralization and crystallization of calcium phosphate in the dental and bone development process, also enhances the differentiation of osteoblasts in cell culture. Additionally, HA coatings with F can provide low enough levels of this element to improve bone formation by enhancing cell attachment [24]. Several studies with HA/F coatings have been published, were the effect of fluorine is assessed as an antimicrobial agent [25, 26].

Results from sputtered HA, HA/F, HA/Ag and HA/F/Ag coatings developed in our laboratory, and never published before, will be presented. Moreover, the incorporation of F is achieved by the co-sputtering from HA and polytetrafluoroethylene (PTFE) targets, while

the introduction of Ag in the nanocomposite is achieved by doping the HA target with one Ag foils (10 × 10 mm), which induces a 8 at.% of silver in the coating. The use of PTFE as fluorine source in hybrid nanocomposites HA-based coatings has never been described in the consulted literature. The deposition parameters were chosen in order to obtain 1 at.% of F in the nanocomposite coatings. This ensures that the amount of released fluorine ions is not toxic for the eukaryotic cells. The coatings were deposited onto 316L stainless steel and Ti cp.

The thickness of all thin films was around 200 nm except for the HA/F/Ag system with 300 nm. The mean surface roughness (Sa), evaluated in the coatings deposited onto polished 316L stainless steel, was around 10 nm for all the coatings, except for the HA/F nanocomposite with a value of 25 nm. Also, the nanocomposite structure of the films was observed by transmission electron microscopy (TEM) (**Figure 6**), where is possible to see, for the HA/F/Ag coating, nanosized silver dispersed onto the amorphous HA and PTFE matrix.

The wettability of the surfaces was evaluated by static contact angle, using water and formamide. The use of two liquids, with distinct surface tensions, allowed to calculate the surface energy (γs) as the sum of its dispersive (γs^d) and polar (γs^p) components [27]. The results in **Table 1** show that regarding the contact angles with water the HA monolithic coating is the more hydrophilic and that both F and Ag addition decrease slightly that characteristic. In what concerns the surface energy of the surfaces, more important than the total value of surface tension is the ratio between its polar and dispersive components. In fact, the polar component gives an idea of the amount of polar groups, with hydrophilic characteristics, which are present.

Of the studied surfaces, the one with the largest polar component is HA. The addition of F, from PTFE target, decreases this value due to known hydrophobic behavior of this polymer. However, its small concentration does not allow for a great decrease in the polar component. The slight decrease of the polar component in the HA/Ag thin film is due to the presence of the metal element having markedly hydrophobic characteristics. However, given that its content
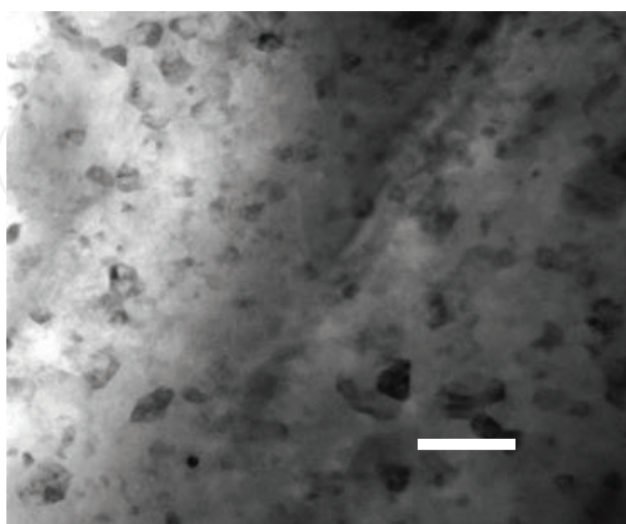

Figure 6. TEM bright field image of HA/F/Ag coating showing the nanocomposite structure of the hybrid sputtered thin film (bar = 100 nm).

Surfaces	Contact angle (°)		Surface energy (mJ.m^{-2})		
	Water	Formamide	γs^d	γs^p	γs
HA	35	15	55.9	8.7	63.6
HA/F	40	41	44.3	8.3	52.6
HA/Ag	50	57	32.3	7.5	39.8
HA/F/Ag	53	29	41.7	7.2	48.9

Table 1. Contact angle and surface energy of the monolithic and HA-based nanocomposites thin films.

in the film is only 8% at, its contribution to the reduction of γs^p cannot be very marked. The HA/F/Ag coating is the one with the greatest decrease in the polar component, since both silver and PTFE contribute to the hydrophobicity.

The surface hydrophilicity and surface charge strongly influences the biological response of a biomaterial, since hydrophilic surfaces do not favor the adsorption of proteins because it is an energetically unfavorable process. The hydrophilicity allows the surfaces to become more efficient in cell attachment, which in this study is important factor since the coatings are designed to induce better osseointegration of implant/bone cells. It is also intended that the coating has a good antibacterial activity, and the free energy of the surface has a significant influence on bacterial adhesion. However, Vogler [28] claims that it is not possible to control the bacterial binding solely by the handling of surface energy. Thus, there is no concrete data to support the claim that a hydrophilic surface is detrimental to good antibacterial activity.

The zeta potential values of the surfaces determined in KCl 1 mM pH 7.4 electrolyte presented very similar values between −81 and −87 mV. These values are more negative than those obtained, for the same electrolyte, with 316L and Ti cp surfaces: −35.8 and −60 mV, respectively. This fact, as explained in the previous section, is very positive as a more negative surface charge implies a better adhesion and proliferation of osteoblastic cells [17].

In order to assess the amount of fluorine release by the HA/F and HA/F/Ag nanocomposites coatings, these samples were immersed, during 30 days in simulated body fluid (SBF) at 37°C with shaking (100 rpm). The fluorine content was measured with a fluorine electrode. The results (**Figure 7**) show, with the help of the trend line, that the amount of fluoride in the solution increase during the first 5 days and after the 10th day the quantity of fluorine in the solution tends to stabilize. The release of F ions is low enough to aid bone formation and at the same time noncytotoxic for the cells.

The antibacterial activity of the coatings were tested by the inhibition growth halo test, which consist of plaiting the selected bacterial strain into solid agar plates with the appropriate culture medium. The surfaces are then placed in contact with the plated microorganism and, after incubation, the plates are observed to see the existence, or absence, of a halo around the tested sample. Its presence indicates that the bacteria did not grow due to the antibacterial effect of the tested sample. In this study, the deposited monolithic and nanocomposite surfaces were tested against *Staphylococcus epidermidis*, a known Gram-positive bacteria.

The results revealed that, after 24 h of incubation, only the surfaces with Ag gave rise to the appearance of an inhibition growth halo, which was bigger in HA/Ag than for HA/F/Ag, 2.6 and 1.4 mm, respectively. The absence of inhibition halo around the samples with fluorine (HA/F) was surprising as this element is cited as an antibacterial agent. The surfaces were then observed by scanning electron microscopy (SEM) (**Figure 8**).
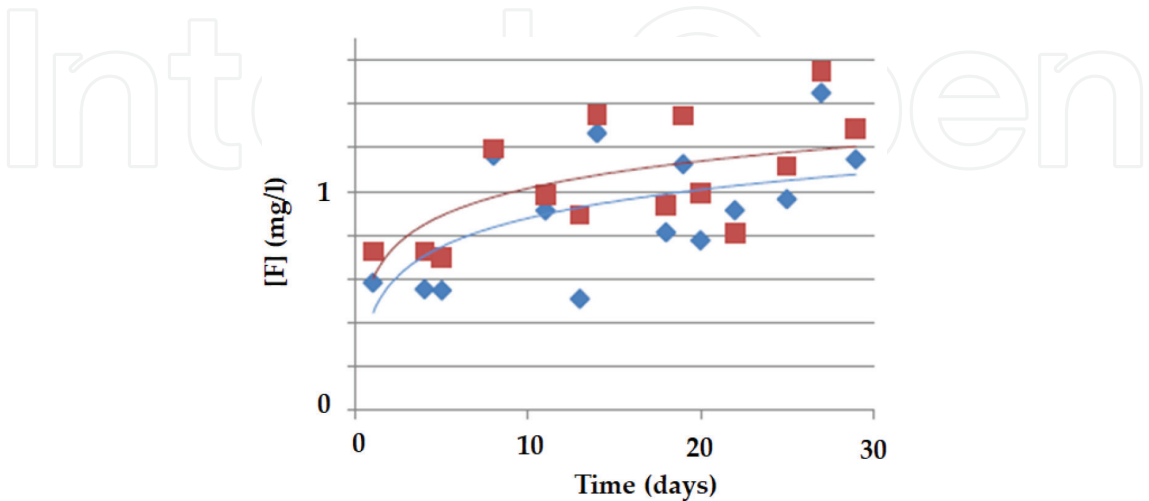

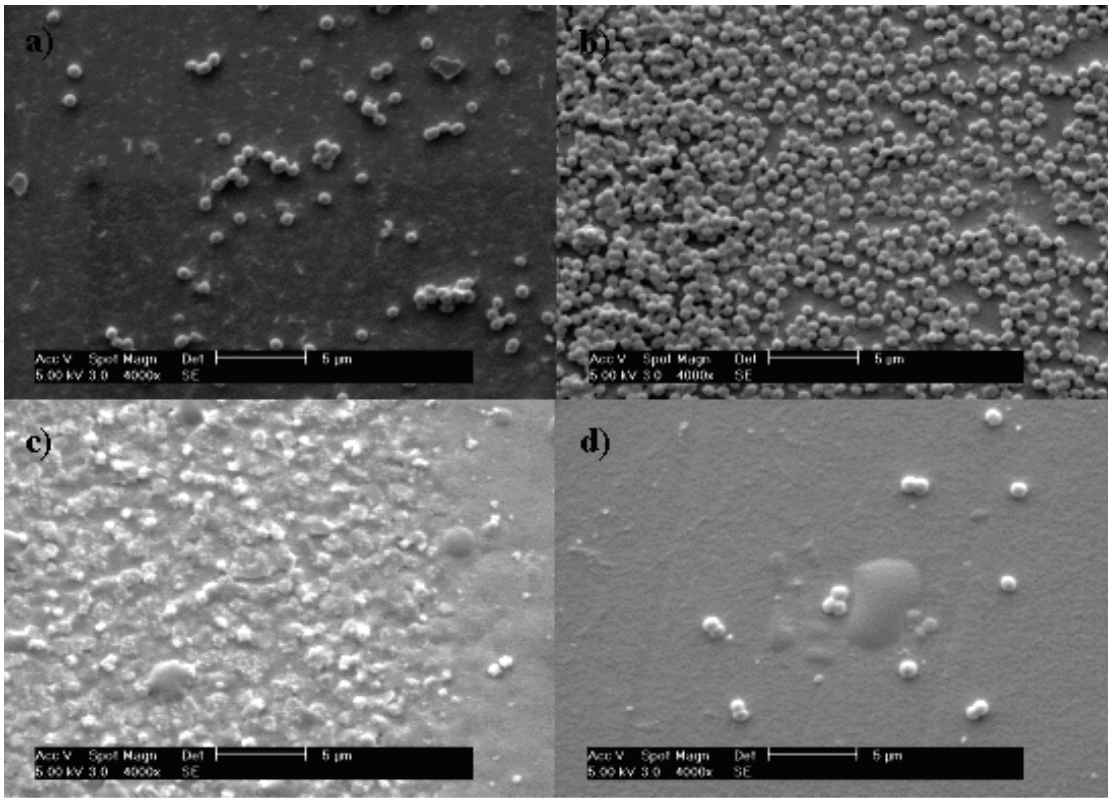**Figure 7.** Release of fluorine from HA/F (blue) and HA/F/Ag (red).

Figure 8. SEM micrographs of the surface of the produced coatings after 24 h of contact with *Staphylococcus epidermidis.*

Through this characterization, it was possible to better understand the way bacteria interacted with the different surfaces. It is possible to note that the HA/F surface is the surface with the greater bacteria colonization, which leads to the conclusion that the presence of fluorine in the coating does not induce any inhibition. This observation is in contradiction with some published results [25] where fluoride HA coating presented a higher antibacterial rate than a monolithic HA coating. However, the observations are in accordance with other published research [29] that concluded that the increase of fluoride ions leads to an increase of bacterial adhesion. As expected, the monolithic HA coating did not present any antibacterial activity. For all surfaces, the bacteria retain their morphology, except in the HA/Ag coating, where it is visible cellular matrix, which is a consequence of the loss of cell wall integrity. Thus, the few cells that colonize the surface do not survive.

In summary, in what concerns the antibacterial activity of hybrid nanocomposite sputtered thin films, each system must be designed and thoroughly characterized in order to understand their real ability has an antimicrobial surface. As explained, the literature is contradictory in some of the real effect of the so-called antibacterial chemical elements that are used to develop nanocomposite coatings.

4. Conclusions

Sputtering is a very versatile technology for the production of hybrid nanocomposite thin films. The ability to develop materials that are not predicted by conventional thermodynamics inheres this technology as one of the best for the development of tailor-made surfaces. In this chapter, it has been highlighted this capacity by describing HA-based hybrid nanocomposites that can be designed to increase the osseointegration of metallic materials usually used for implants with contact with biological hard tissue. The HA-based nanocomposites hybrid coatings were also chosen to demonstrate the capacity of developing hybrid ceramic/polymer/metal nanocomposites with good antibacterial activity. The combination of these three types of materials in one surface is almost impossible to obtain, except by the use of the sputtering technique.

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Conflict of interest

The author declares no conflict of interest.

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