



# Strontium-substituted hydroxyapatite coatings deposited via a co-deposition sputter technique



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## ABSTRACT

The bioactivity of hydroxyapatite (HA) coatings can be modified by the addition of different ions, such as silicon (Si), lithium (Li), magnesium (Mg), zinc (Zn) or strontium (Sr) into the HA lattice. Of the ions listed here, strontium substituted hydroxyapatite (SrHA) coatings have received a lot of interest recently as Sr has been shown to promote osteoblast proliferation and differentiation, and reduce osteoclast activity. In this study, SrHA coatings were deposited onto titanium substrates using radio frequency (RF) magnetron co-sputtering (and compared to those surfaces deposited from HA alone). FTIR, XPS, XRD, and SEM techniques were used to analyse the different coatings produced, whereby different combinations of pure HA and 13% Sr-substituted HA targets were investigated. The results highlight that Sr could be successfully incorporated into the HA lattice to form SrHA coatings. It was observed that as the number of SrHA sputtering targets in the study were increased (increasing Sr content), the deposition rate decreased. It was also shown that as the Sr content of the coatings increased, so did the degree of preferred 002 orientation of the coating (along with obvious changes in the surface morphology). This study has shown that RF magnetron sputtering (specifically co-sputtering), offers an appropriate methodology to control the surface properties of Sr-substituted HA, such as the crystallinity, stoichiometry, phase purity and surface morphology.

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## 1. Introduction

The nature of the initial interaction between calcium phosphate (CaP) thin films and osteoblasts can be mediated by the outermost surface properties of that material. As such, the phase, crystallinity, stoichiometry, composition and morphology of the CaP surfaces are seen as key parameters that must be accurately controlled in order to influence their potential biofunctionality with respect to osteoblasts. Hydroxyapatite [HA–Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] has been extensively studied due to the structural and chemical similarities demonstrated with the main inorganic constituent of bone tissue and teeth. However, it is well documented that biological hydroxyapatite, which forms the mineral phases of calcified tissues (enamel, dentin and bone), differ from pure and synthetically produced HA. Biological apatite is comprised of a mixture of calcium phosphate phases, such as tricalcium phosphate (TCP), carbonated hydroxyapatite (CHA) and calcium-deficient hydroxyapatite (CDHA). In this regard, synthetic HA exhibits a Ca/P ratio of 1.67, whereas biological apatite deviates significantly from this value and are known to be

calcium-deficient (Ca<sub>(10-x)</sub>(HPO<sub>4</sub>)<sub>x</sub>-(OH)<sub>2-x</sub>), with a Ca/P ratio which can be as low as 1.5 [1]. Numerous impurities such as fluoride, magnesium, sodium, potassium, carbonate and chloride can also be found in naturally occurring bone. In addition to this trace amounts of elements such as strontium, barium, copper, zinc, and iron are commonly associated with biological apatite and may be seen as substituents in the apatite structure [2]. Therefore, one approach to control the osteoblastic response of HA coatings, both in vitro and in vivo, could involve the use of substituted HA, incorporating different ions, such as silicon (Si) [3], lithium (Li) [4] magnesium (Mg) [5], carbonate (CO<sub>3</sub>) [6], zinc (Zn) [7], silver (Ag) [8], fluoride, (F) [9], chloride (Cl) [10], potassium (K) [11], copper (Cu) [12], sulphate (SO<sub>4</sub>) [13], tantalum (Ta) [14], cerium [15] or strontium (Sr) [16] into the HA lattice, in order to mirror the complex chemistry of human bone. Many reports of the use of these substituted materials can be found in the literature, both as bone substitute materials and as coatings [17–19]. Of the different substitutions listed above, strontium substituted hydroxyapatite (SrHA) coatings have received a lot of interest recently as strontium (Sr) has been shown to have the dual benefit of promoting bone formation and reducing bone resorption, in vivo. Furthermore, it has been shown that strontium has the ability to enhance pre-osteoblastic cell replication, to activate the Wnt/ $\beta$ -caterine signalling pathway that will therefore stimulate the formation of new bone through osteogenesis and differentiation into osteoblasts [20–23]. It has also been shown in a number of other studies [24,25] that strontium has the ability

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to inhibit the activity of osteoclasts. It has been reported that the optimum strontium concentration for enhanced osteoblast activity, including proliferation and differentiation could be observed when the substitution of strontium into HA was at a high level of 3–7% [26].

A number of different deposition methods have been investigated to deposit Sr-substituted HA surfaces, including Radio Frequency (RF) magnetron sputtering [16], plasma spraying [27], sol–gel methods [28], pulsed laser deposition [29], micro-arc oxidation [30] and co-blasting [17]. Of the methods highlighted here, RF magnetron sputtering has been shown to be particularly useful for the deposition of Ca–P coatings due to the ability of the technique to provide greater control of the coating's properties, along with improved adhesion between the substrate and the coating [30–32]. Specifically, RF magnetron sputtering allows co-deposition of multiple target materials simultaneously and provides an alternative and simple method to produce Sr-substituted HA coatings [32]. A previous study by Ozeki et al. focused on the deposition of Sr-substituted HA coatings, albeit it using a single sputtering target of mixed composition (Sr-substituted HA powder) [16]. To date, however, to the best of the authors' knowledge, there is no available information on the utilisation of co-sputter deposition as a method to deposit Sr-substituted HA surfaces using RF magnetron sputtering, with the primary objective of creating a surface with specific surface chemistry and morphology commensurate with enhanced biofunctionality.

The present work was undertaken in order to study the co-sputter deposition of Sr-substituted coatings from a custom designed RF magnetron sputtering facility utilising three sputtering targets (referred to as sources). In particular, the influence of different target compositions and configurations on the properties of the Sr-substituted sputter deposited coatings produced at a low discharge power level (150 W) were investigated. A low discharge power level was chosen for this study as the quality and consistency of the targets used could be guaranteed throughout the sputter deposition runs. All of the coatings produced were characterised after post-deposition annealing to 500 °C using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and stylus profilometry.

## 2. Materials and methods

### 2.1. Substrate preparation

For this study coupons of chemically pure titanium (cpTi), Titanium International Ltd (15 mm × 15 mm × 0.5 mm) were abraded using a succession of 800, and 1200 grade SiC papers. The coupons were twice sonicated for ten minutes consecutively in acetone, isopropyl alcohol and distilled de-ionised water. The abraded coupons were then dried thoroughly in a convection oven at 70 °C for twelve hours.

### 2.2. Sputtering procedure

Sputtering targets, 76 mm in diameter and 5 mm thick, were produced by dry pressing hydroxyapatite [HA – (Plasma Biotol Capital-R)] and 13% Biphasic Calcium Phosphate [SrHA – (Himed Inc. NY, USA)] powders (at a load of 40 kN for 10 min with a loading rate of 10 kN per minute). RF magnetron sputtering was performed using a cluster of three high vacuum Torus 3 M sputtering sources in a custom designed system (Kurt J. Lesker Ltd, USA) each operating with a 13.56 MHz RF generator and an impedance matching network (Huettinger, GmbH, Germany). The sources were all mounted at 65° to the substrate surface. For deposition from the sputtering targets onto the cpTi substrates, the RF power in the sputtering system was ramped up slowly to provide an initial break-in phase, thereby minimising any thermal shock effects. The break-in prior to deposition from the HA target was conducted at a ramp rate of 5 Watts (W) per minute (all with the source shutter closed). The base pressure was below  $5 \times 10^{-6}$  Pa, with an argon gas flow rate (BOC, 99.995%) of between 15–20 Sc cm and a throw distance

of 100 mm. To produce the co-deposited coatings with different levels of Sr-substitution, targets combinations in the three source multi-target configuration were utilised as outlined in Table 1. The fragility of the HA and 13SrHA targets limited their power absorption capacity and consequently deposition was performed at 150 W for 5 h under the same atmospheric conditions as were used for the target break-in procedure. The power density for these HA targets was approximately  $3.3 \text{ W cm}^{-2}$ . After sputter deposition, the Ca–P coatings were thermally annealed in order to enhance their crystallinity. The samples were subjected to a ramp rate of 5 °C per minute to 500 °C (from room temperature) with a soak time of 2 h and a ramp rate of 5 °C per minute back down to room temperature.

### 2.3. Characterisation of the Ca–P powders and coatings

Fourier Transform Infrared (FTIR) spectroscopy of the samples was carried out using a BIORAD FTS 3000MX Excalibur series instrument with a PIKE Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) accessory. Samples were analysed from  $4000\text{--}400 \text{ cm}^{-1}$  in absorbance mode at a resolution of  $4 \text{ cm}^{-1}$  with 20 scans per sample.

X-Ray Diffraction (XRD) of the samples was performed using a Bruker D8 Discover Diffractometer fitted with a Gobel Mirror. A Cu K $\alpha$  X-Ray radiation ( $\lambda = 1.540 \text{ \AA}$ ) source was employed with diffraction scans obtained at a tube voltage of 40 kV and a tube current of 40 mA. Each diffraction scan was recorded at 2 $\theta$  values from 20–50° with a step size of 0.04° and a scan dwell time for each increment of 30 s. For the grazing incidence angle XRD studies of Ca–P coatings on the cpTi substrates the tube angle was set to 0.75°.

X-Ray Photoelectron Spectroscopy (XPS) of the samples was undertaken using a Kratos Axis Ultra DLD spectrometer. Spectra were recorded by employing monochromated Al K $\alpha$  X-Rays ( $h\nu = 1486.6$  electron volts (eV)) operating at 5 kV and 15 mA (75 W). The base pressure was  $1.33 \times 10^{-7}$  Pa and the operating pressure was  $6.66 \times 10^{-7}$  Pa. A hybrid lens mode was employed during analysis (electrostatic and magnetic), with an analysis area of approximately  $300 \mu\text{m} \times 700 \mu\text{m}$  and a take-off angle (TOA) of 90° with respect to the sample surface. Wide energy survey scans (WESS) were obtained at a pass energy of 160 eV. High resolution spectra were recorded for O1s, Ca2p and P2p and C1s (incorporating the Sr3p peak) at a pass energy of 20 eV. The Kratos charge neutraliser system was used on all samples with a filament current of 1.95 A and a charge balance of between 3.3 and 3.6 V. Sample charging effects on the measured BE positions were corrected by setting the lowest BE component of the C1s spectral envelope to 285.0 eV, i.e. the value generally accepted for adventitious carbon surface contamination [34]. Photoelectron spectra were further processed by subtracting a linear background and using the peak area for the most intense spectral line of each of the detected elemental species to determine the % atomic concentration.

The deposition rate (and thickness) of the different Ca–P coatings were determined using a Dektak 8 stylus profilometer (Veeco Instruments Inc., USA). Measurements were taken across 10 step height positions on each sample created by masking titanium coated silicon substrates with aluminium foil prior to deposition in the sputtering system. A 12.5  $\mu\text{m}$  diameter diamond tipped stylus was employed with scans lengths of 1000  $\mu\text{m}$  at a load of 15 mg.

**Table 1**  
Target configuration versus coating thickness.

Target configuration	Coating thickness (nm)
3 HA	445 ± 16
2HA/1SrHA	341 ± 17
1HA/2SrHA	248 ± 14
3SrHA	204 ± 11

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