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Crystalline nano-coatings of fluorine-substituted hydroxyapatite produced by magnetron sputtering with high plasma confinement

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ABSTRACT

A radio-frequency magnetron sputtering technique operating in right-angle geometry (RAMS) with high plasma confinement was revised to produce thin films (15–570 nm) of fluorine-substituted hydroxyapatite, FHA, adapted to be used as nano-coatings for biomedical implants. An electron temperature of $T_{eff} \approx 9.0$ eV and a plasma electron density of 1.2×10^{15} m^{-3} assured the nucleation of an amorphous fluorine-substituted hydroxyapatite phase on Si and Ti surfaces. With the aid of a Langmuir probe, the RAMS plasma energy was tuned to control the coating stoichiometry and the ratio between the crystalline and amorphous phases. The energy delivered over time from the bombardment of ions and electrons transformed the amorphous calcium phosphate phase into crystalline fluorine-substituted hydroxyapatite. The crystalline films were obtained at room temperature. The partial substitution of OH^- for F^- in the HA structure was confirmed by X-ray diffraction using synchrotron radiation in grazing-incidence mode, X-ray photoelectron spectroscopy and attenuated total reflection Fourier transform infrared spectroscopy. High-resolution transmission electron microscopy carried out on cross-section film samples prepared by a focused ion beam (FIB) technique revealed that the film ultrastructure was composed of columnar crystals oriented perpendicularly to the substrate surface. The crystals were connected to the substrate surface by ordered nanolayers, indicating the existence of a continuous binding between the two materials. This work demonstrates that the RAMS technique is able to produce FHA nano-coatings with controlled chemical compositions and structures on metallic implants for clinical applications.

1. Introduction

Hydroxyapatite (HA) is one of the most important biomaterials for bone regeneration and drug delivery [1,2]. HA has been used as a bioactive coating to improve the osteoconductivity of metallic implants. In addition to plasma spray deposition, a large number of coating techniques have been proposed for HA deposition on titanium implants, such as the sol-gel process [3], electrodeposition [4], pulsed laser deposition (PLD) [5], electron and ion beam deposition [6,7], electron-cyclotron-resonance (ECR) [8], and radio-frequency magnetron sputtering (RFMS) [9].

One challenge faced in materials science is to produce a coating that is stable and osteoconductive in a biological medium [10]. The deposition technique applied should be capable of producing adherent, crystalline and stoichiometric coatings on an implant surface. In recent years, deposition techniques have been adapted to produce thin coatings with thicknesses less than 500 nm to improve substrate adhesion and to preserve the original topography of a metallic implant [11]. However, it is difficult to produce a thin coating without the formation of undesirable and amorphous phases [12–16]. Coatings are generally treated at temperatures of up to 900 °C to transform amorphous phases into HA [8,15,16]. However, this thermal treatment may produce undesirable phases such as tricalcium phosphate (α,β –TCP) and calcium oxide (CaO) and cause the coatings to crack [6,8,12,15–18]. HA coatings with ionic substitutions have been produced to stimulate bone binding to an implant surface. The substitution of Zn^{2+} and Sr^{2+} for Ca^{2+}, the substitution of SiO_4^{4-} and CO_3^{2-} for PO_4^{3-} and the substitution of F^- for OH^- have been shown to stimulate bone cell adhesion to an implant and to enhance the stability of coatings [19–21]. The incorporation of F^- into the HA structure reduces the lattice parameters and the unit cell volume, resulting in a structure with a higher hardness and a lower dissolution rate [22,23]. Therefore, one way to increase the structural stability of an HA coating and decrease its in vivo dissolution rate is to partially substitute F^- for OH^- ions (i.e., $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$; FHA). In vitro studies have shown that this substitution induces greater cell proliferation [16,24] and reduces bacterial proliferation [25]. These results suggest that the incorporation of fluorine into the HA structure could be used as an alternative route to improve the mechanical and biological behaviour of apatite coatings in metallic implants for biomedical applications.

FHA coatings have been produced by different methods, such as thermal spray deposition, electrodeposition, the sol-gel process and

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Table 1
FHA film series and deposition parameters.

Series	Ar pressure (Pa)	O_2 pressure (Pa)	RF power (W)	Dep. time (min)	Height (Z) (mm)	Dep. rate (nm/min)	Substrate[1]
1st	0.67	0.13	90, 100, 110, 120	180	29	--	Si(100)
2nd	0.67	0.13	110	5,10,15,20,25,30,...,180	29	3.0	Si(100)
3rd	0.67	0.13	110	60	29	3.0	Si(100)
4th	0.67	0.13	110	15,30,45,60,90,120,150,180	29	3.0	Si(100)/Ti

[1] All the silicon substrate wafers were oriented at (100) and type P doped.

laser pulse deposition [14,16,26–32]. However, these techniques present their own challenges with respect to i) control over fluorine incorporation into the HA structure and ii) the crystalline structure of FHA coatings. The latter issue depends on whether thermal treatments are performed during or after the deposition process [10,15,16]. In general, these deposition techniques produce micron-thick FHA coatings (i.e., >1 μm). There are few published studies focusing on the production of thin films from partially fluorinated HA, especially by radio-frequency magnetron sputtering (RFMS) [16].

Recently, E.O. López [33] developed a right-angle radio-frequency magnetron sputtering (RAMS) technique to produce thin HA films. The geometry of the magnetron sputtering was altered to increase the magnetic confinement and the RF plasma energy. With these changes, the authors increased the deposition rate to produce thin, stoichiometric crystalline HA films on silicon and titanium substrates at room temperature. In the present work, we used the RAMS technique to produce thin coatings of fluorine-substituted hydroxyapatite (FHA; measuring less than 500 nm in thickness). The plasma energy and deposition parameters were tuned to control the film stoichiometry and crystallinity. Surface and bulk techniques were used to characterise coating growth during the deposition process and the incorporation of fluorine into the HA structure.

2. Experimental section

2.1. Target and substrate preparation

Fluorine incorporated into HA (FHA), $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$ ($0 < x < 2$), where $x = 0.6$, was synthesised according to the procedure described by Rodríguez [34]. A tetrahydrated calcium nitrate solution ($Ca(NO_3)_2 \cdot 4H_2O$) was dropped into a solution of diammonium phosphate ($(NH_4)_2HPO_4$) and ammonium fluoride (NH_4F) under stirring at 90 °C and pH = 9. After the addition of reagents, the precipitate was stirred for 4 h. The solid was then washed and dried at 80 °C for 24 h.

Targets measuring 35 mm in diameter and 3.5 mm in height were produced by uniaxially pressing the synthesised FHA powder at 51 MPa. After pressing, FHA pellets were sintered at 1100 °C for 2 h. The films were deposited on silicon (100) substrates and silicon (100) substrates coated with titanium (Si/Ti). The silicon substrates were cut into smaller substrates with dimensions of 11 mm × 11 mm, washed with deionised water, neutral detergent and acetone and ultrasonicated for 10 min. Metal oxides on the substrate surface were removed by treating the substrates with a 5% solution of hydrofluoric acid (HF) in deionised water for a maximum duration of 1 min. Afterward, the substrates were rinsed with deionised water and dried with dry nitrogen gas under high pressure.

2.2. The RAMS system and plasma characterisation

The RAMS system used in this work had the same setup as that described elsewhere [33,35]. It was composed of two magnetrons positioned face-to-face operating at 13.56 MHz. The substrate holder was positioned at a distance Z from the centre of the magnetrons. The radio-frequency (RF) power was coupled to a matching network to achieve power densities of up to 26.0 W/cm^2. The magnetron system generated a magnetic field inside the sputtering chamber that confined electrons with high kinetic energy. A strong magnetic field ($\mathbf{B}$ = 0.143 T) at a moderate distance from the targets was created by two NdFeB magnets (N40 grade). To ensure the stability of the magnetic field, the magnetrons were water-cooled at 18 °C.

The substrate holder was positioned at a right angle to the magnetrons and isolated from the sputtering chamber. The floating potential of the substrate holder was used to improve thin-film crystallinity [33,35]. Plasma energies at different distances from the substrate position (Z = 29 mm) were evaluated by a Langmuir probe. Measurements were conducted using 110 W of RF power and Ar and O_2 pressures of 0.67 Pa and 0.13 Pa, respectively. The Langmuir probe consisted of a tungsten tip and a circuit set at a filtering frequency of 13.56 MHz. The probe tip (800 μm in diameter and 3.5 mm in length) was connected to a DC source ($-100\ V < V_b < 100\ V$) that polarised the tip when it was inside the plasma. The interaction of the plasma with the tip probe produced a region of charged and neutral particles

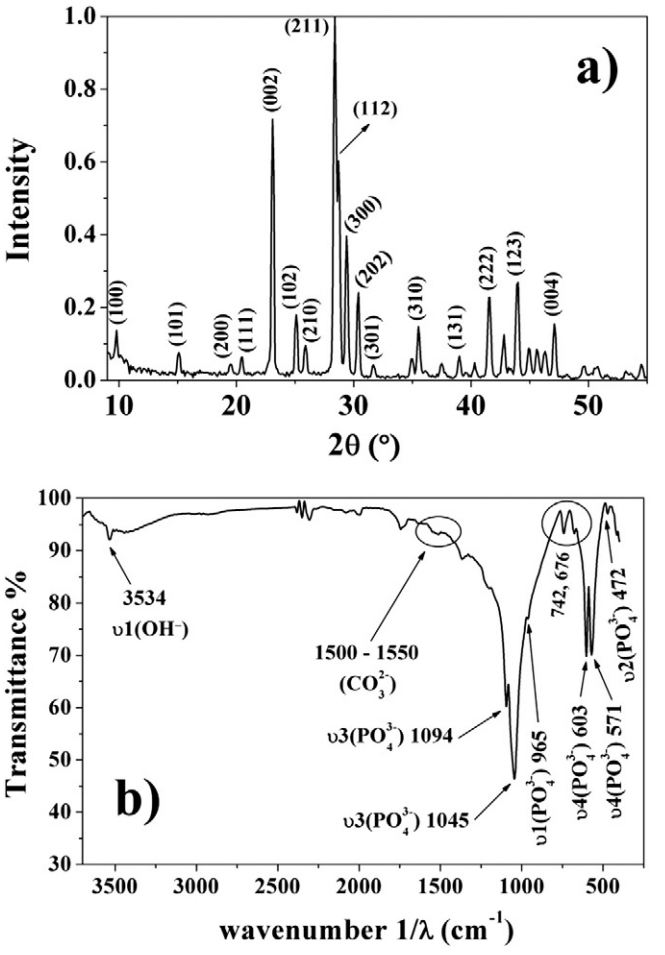

Fig. 1. (a) XRD (λ = 0.1377 nm) patterns and (b) FTIR spectrum of FHA targets sintered at 1100 °C for 2 h.