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The Influence of argon gas pressure on co-sputtered calcium phosphate thin films

A.R. Boyd *, H. Duffy, R. McCann, M.L. Cairns, B.J. Meenan

Nanotechnology and Integrated Bioengineering Centre (NIBEC), University of Ulster at Jordanstown, Shore Road, Newtownabbey, Co. Antrim, BT37 0QB. Northern Ireland, UK

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Abstract

A series of Ca–P coatings have been co-deposited by RF magnetron sputtering from hydroxyapatite targets at a range of different argon gas pressures (1–5 Pa) at a low discharge power level. The resultant surfaces were analysed both as-deposited and after annealing at 500 °C using fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and stylus profilometry. The deposition rate increased with increasing argon gas pressure up to 2 Pa, but decreased significantly as the pressure increased up to 5 Pa. The Ca/P ratios of the as-deposited coatings were lower than expected, and decreased significantly at the higher argon gas pressures. The corresponding FTIR and XRD data showed that the as-deposited surfaces were poorly hydroxylated and were mostly amorphous in nature. By comparison, the annealed surfaces had Ca/P ratios of between 3.38 ± 0.11 (1 Pa) and 1.82 ± 0.06 (5 Pa). The FTIR and XRD data for the annealed samples were indicative of HA, however, as the gas pressure increased above 3 Pa, these surfaces were most likely transformed into dehydroxylated HA. This study has shown the utility of varying the argon gas pressure whilst co-sputtering HA in order to modify the resultant surface conditions.
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1. Introduction

The ability to carefully manage cell–surface interactions by the deliberate modification of a biomaterial's surface properties is seen as a key route for harnessing the appropriate responses for tissue regeneration and repair. In this regard calcium phosphate (Ca–P) bioceramics and in particular those based on hydroxyapatite [HA–$(Ca_{10}(PO_4)_6(OH)_2)$], have been studied extensively as coatings for hard tissue implant applications due to their osteoconductive properties [1]. In order to produce Ca–P surfaces that exhibit the appropriate surface cues for enhanced biofunctionality, many different deposition techniques have been investigated, including radio frequency (RF) magnetron sputtering, which has demonstrated a great deal of potential in this area [2–8]. Many different aspects of the sputtering process have been investigated in order to provide optimised surface conditions, including RF discharge power [3], argon gas pressure [4,9], gas composition [6] and target surface conditions [10]. Experiments that have been conducted at high discharge power levels (200–800 W) have often utilised plasma sprayed targets, due to the poor mechanical integrity exhibited by dense sintered targets or dry pressed targets during the sputtering process [3]. However, the plasma sprayed targets were found to contain additional Ca–P phases other than

* Corresponding author. Tel.: +44 02890 368924; fax: +44 02890 366863.
E-mail address: ar.boyd@ulster.ac.uk (A.R. Boyd).

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hydroxyapatite, and as a result their consistency and that of the resultant coatings could not be assured [2–8]. In order to prevent this inconsistency an approach of utilising dry pressed targets [10,11] or dense sintered targets [9] at low discharge power levels (<150 W) has been adopted. Indeed, coatings produced from such systems have been shown to contain only hydroxyapatite and no other additional Ca–P phases or by-products [10,11]. However, the as-deposited coatings are normally amorphous in nature and require thermal processing in order to enhance their crystallinity. To date most of the studies reporting on the deposition of Ca–P coatings by RF magnetron sputtering have utilised a single Ca–P target, however, recent studies have demonstrated how co-sputtering from two targets could be successfully applied to produce silicon containing HA surfaces [12,13]. Despite this there is little other information available on the utilisation of multiple HA targets to co-sputter Ca–P surfaces with the appropriate surface functionality. Therefore, the present work was undertaken in order to study the co-deposition of Ca–P coatings from three HA targets and report on its potential utility. In particular, the influence of the argon gas pressure on the properties of Ca–P coatings produced at a low discharge power level (150 W) was 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 in the as-deposited (AD) state and after post-deposition annealing (PDA) at 500 °C using fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and stylus profilometry.

2. Materials and methods

2.1. Substrate preparation

Coupons of 316 L stainless steel (Goodfellows Ltd. (UK)) ($10 \times 10 \times 1$ mm) were abraded using a succession of 500, 800, and 1200 grade SiC papers. The coupons were twice sonicated in isopropyl alcohol (AnalaR Grade, BDH) for 10 min and twice in de-ionised water for 10 min. The abraded coupons were then dried thoroughly in a convection oven at 120 °C for 2 h prior to sputter deposition.

2.2. Sputtering procedure

HA targets, 76 mm in diameter and 5 mm thick were produced by dry pressing HA powder (Merck KGaA, Darmstadt, Germany) 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 45° to the substrate surface. For deposition from the HA targets onto the stainless steel 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 7×10^{-5} Pa, with an argon gas flow rate (BOC, 99.995%) of between 15–18 Sccm and a throw distance of 100 mm. A series of coatings were produced in this study by varying the argon gas pressure between 1–5 Pa. The fragility of the HA 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 W cm^{-2}. After sputter deposition, the Ca–P coatings were thermally annealed. 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 coatings

Fourier transform infrared (FTIR) spectroscopy of the samples were 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 4000–400 cm^{-1} in absorbance mode at a resolution of 4 cm^{-1} with 20 scans per sample.

X-Ray diffraction (XRD) of the samples were carried using a Bruker D8 Discover Diffractometer fitted with a Gobel Mirror. A Cu Kα X-ray radiation ($\lambda = 1.540$ Å) 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 2θ values from 20–40° 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 stainless steel substrates the tube angle was set to 0.75°.

X-Ray photoelectron spectroscopy (XPS) of the samples were carried out using a Kratos Axis Ultra DLD spectrometer. Spectra were recorded by employing monochromated Al Kα X-rays ($hv = 1486.6$ electron volts (eV)) operating at 5 kV and 15 mA (75 W). The base pressure was 1.33×10^{-7} Pa and the operating pressure was 6.66×10^{-7} Pa. A hybrid lens mode was employed during analysis (electrostatic and magnetic), with an analysis area of approximately 300 μm × 700 μm and a take off angle (TOA) of 90° with respect to the sample surface. Wide energy survey scans (WESS) were obtained over the range 0–1200 eV binding energy (BE) at a pass energy of 160 eV. High resolution spectra were recorded for C1s (278–295 eV), O1s (525–540 eV), Ca2p (340–362 eV) and P2p (125–140 eV) at a pass energy of 20 eV. The Kratos charge neutraliser system was used on all samples with a filament current of 1.8 A and a charge balance of 3.6 V. Sample charging

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