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Nanomechanical characterization of bioglass films synthesized by magnetron sputtering

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ABSTRACT

Bioactive glasses are osteoproductive-type inorganic materials possessing the highest indices of bioactivity in both bulk and thin film forms. The prerequisites for reliable implant-type coatings are both their biological and mechanical performances. Whilst the bioglass films' structural, chemical and biological properties have been studied extensively, information about their mechanical performance is scarce. Here, transmission electron microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, nanoindentation and pull-out measurements were employed to assess the morphological, chemical, structural and mechanical properties of the bioglass films deposited onto Ti substrates by radio-frequency magnetron sputtering (RF-MS). The biological safety of the thin bioglass films was evaluated preliminarily in vitro by investigating the adherence, proliferation and cytotoxicity of fibroblast cells cultivated on their surface. Our study emphasize the versatility of RF-MS, showing how bioglass films' features such as composition, structure, bonding strength, hardness, elastic modulus and biological response can be conveniently adapted by tuning the RF-MS working conditions, and therefore demonstrating the unexplored potential of this deposition technique for preparing quality biomimetic glass coatings.

1. Introduction

Nowadays, bioengineering has greatly expanded towards the study of biocompatible materials in the form of thin films. As a consequence, the coating of biotolerated/bioinert metallic implants with bioactive materials, able to induce a rapid osteointegration, has been envisaged for the development of medical devices.

Bioglasses (BG) are materials known to possess the higher indices of bioactivity, and since their discovery [1] many compositional systems have been proposed and proved their suitability to form a strong bond with living tissues [2]. But their intrinsic low mechanical properties have mitigated their application in medical practice. In order to address these shortcomings, bioglass thin films were attempted as alternative solutions to hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] coatings but have achieved limited success [2,3]. Bioglass-derived implant coatings are not yet commercially available.

An important number of deposition techniques have been tried in the attempt of producing BG films reliable for implatology [3]. Radio-frequency magnetron sputtering (RF-MS) allows the synthesis of high purity uniform films on large area substrates, having complex 3D geometries [4], allowing also an easy and efficient technological transfer to industry, as proved in the past in decorative and semiconductor manufacturing. Moreover, RF-MS is widely acknowledged for producing films with good adherence to the substrate and a density close to bulk (target) material [4,5].

Whilst the scientific literature abounds with structural, chemical and biological properties of bioglass films, information about their mechanical performance, essential for load-bearing biomedical applications, is scarce [6–9].

The aim of this work was to synthesize quality BG coatings by this promising alternative deposition method (RF-MS) and to employ a multi-parametrical evaluation to assess their morphological, chemical, structural, mechanical and biological properties. The study discloses how essential properties of BG films such as composition, structure, bonding strength, hardness, elastic modulus or cytocompatibility, can be tailored by suitably adjusting the sputtering conditions. The relationships between the physico-chemical features of BG films and their mechanical and biological responses are discussed.

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2. Experimental procedure

2.1. Powder preparation

A bioactive glass composition (wt.%: SiO_2 — 46.06, CaO — 28.66, Na_2O — 4.53, P_2O_5 — 6.22, MgO — 8.83, and CaF_2 — 5.70) was recently developed [10] and tailored to obtain a thermal expansion coefficient of around $10.44\times10^{-6}\,°C^{-1}$, close to that of titanium (Ti) and its alloys ($9.2–9.6\times10^{-6}\,°C^{-1}$), in the temperature range of 200–400 °C. Powders of technical grade (purity > 99.5%) of SiO_2 and $CaCO_3$ and of reagent grade of $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$, Na_2CO_3, CaF_2, and $NH_4H_2PO_4$ were used for the BG preparation. The homogeneous batches (~100 g) prepared by ball milling in ethanol were preheated at 1000 °C for 1 h for complete decarbonisation and then melted in Pt crucibles at 1400 °C for 1 h in air. Glass frit, obtained by quenching the melt into cold water, was dried and milled in a high-speed porcelain mill. The milled frit was passed through a sieve to obtain a fine powder with a mean particle size of about ~20 μm (as estimated by light scattering technique, using a Coulter LS 230 particle size analyser, and applying the Fraunhofer optical model).

Bioglass targets (110 mm diameter, 3 mm thick) were manufactured by cold pressing from as-prepared powders [11,12]. Polished square pieces of Ti grade 1 (Mateck GmbH), having an area of 1 cm^2, were used as substrates. The substrates were ultrasonically cleaned successively in acetone and ethanol for 10 min in an ultrasonic bath before being mechanically fixed into the deposition chamber in an aluminium holder at a target-to-substrate distance of 25 mm.

2.2. Deposition procedure

BG films were sputtered using a UVN-75R1 (1.78 MHz) deposition system. The sputtering chamber was first evacuated to a pressure less than 2×10^{-3} Pa. Then argon and oxygen, of purity grade 6.0 (99.9999%), were admitted through needle valves at various flow rates in order to obtain the desired deposition atmospheres at various oxygen dilutions and total pressures (Table 1). A long pre-sputtering time (10 min at 0.3 Pa pure argon pressure, and 50 min in the exact deposition condition) was used to assure a clean target surface and a stable sputtering process. Prior to deposition, the Ti substrates were plasma etched in argon atmosphere for 10 min, aiming at improving the films' adhesion, using the procedure proposed in Ref. [13]. Other specific deposition parameters are listed in Table 1.

2.3. Characterization techniques

i) Spectroscopic ellipsometry was employed to determine the deposition rate on silicon substrates for each set of deposition conditions. The measurements were performed using a J.A. Woollam Co. Variable Angle Spectroscopic Ellipsometer in the 1.2–4 eV spectral range, step 0.01 eV, at 3 angles of incidence: 45°, 60° and 75°. The experimental spectra were fitted with a 3 layer optical model: Si substrate, SiO_2 native oxide (3 nm) and the sputtered BG thin film. For the deposited layer a Cauchy dispersion was used [14,15]. The thickness errors given by the Woollam's analysis software are within 1 nm. The as determined deposition rates were used to deposit films of equal thickness (~1 μm) onto Ti substrates reported in this manuscript.

ii) Information on bonding configuration in the bioglass powder and in the as-deposited coatings was obtained by Fourier transform infrared (FTIR) spectroscopy, using a Perkin Elmer BX Spectrum-Pike spectrometer in attenuated total reflection mode (Pike-MIRacle Diamond Head). The analysis was performed within the range 550–4000 cm^{-1}, at a 4 cm^{-1} resolution, with a total of 50 scans per experiment.

iii) In order to gain a better insight into the chemical bonding structure at the surface of BG films, X-ray photoelectron spectroscopy (XPS) analyses were performed. A dedicated surface science facility (SPECS) was used to conduct the XPS measurements whilst keeping the base pressure below 10^{-8} Pa. The spectra were recorded using the Al $K_{\alpha1}$ monochromatised radiation (E = 1486.74 eV) in an analysis chamber equipped with a 150 mm hemispherical electron energy analyser (Phoibos) operating in fixed analyser transmission mode with pass energy of 20 eV and step energy of 0.05 eV. The estimated combined (source + analyser) resolution was about 0.75 ± 0.025 eV. In order to prevent an eventual drift of the XPS lines, the sample neutralization during measurements was attained by using a flood gun operating at an acceleration energy of 1 eV and an electron current of 100 μA. This was systematically checked on C 1s spectra on reference samples (284.5 eV) and the observed energy shifts were always lower than 0.1 eV.

iv) The cross-sectional transmission electron microscopy (XTEM) analyses were carried out with a JEOL 200CX electron microscope operated at 200 kV. The thin lamella for XTEM observation has been prepared by Focused Ion Beam (FIB) techniques using a Tescan Lyra III scanning electron microscope-FIB dual system provided with a gallium liquid metal ion source operated at 30 kV. The ion probe current was 20 nA during early stages of rough milling and reduced to 10 pA for the final polishing.

v) The average composition of the BG films was estimated by energy-dispersive X-ray spectroscopy (EDS) measurements performed with a Bruker QUANTAX 400 EDS instrument. For experimental reproducibility, the EDS analyses were performed in duplicate, making measurements on five different regions of 500 μm^2. The results were analysed separately, and both sets of experiments had comparable results. For this reason only results from one of the two sample batches are presented in the article.

vi) Pull-out measurements were carried out using a DFD Instruments PAT MICRO AT101 (maximum pull force = 1 kN) adhesion tester equipped with 2.8 mm diameter stainless steel test elements. The experimental procedure was conducted in accordance with the ASTM D4541-09e1 standard, as described elsewhere [11]. Ten samples were tested independently for each type of deposition condition. Mean values and standard deviations were computed.

vii) The nanoindentation measurements were performed using a Micro Materials Nanotest platform equipped with a Berkovich indenter. The load partial–unload method was used in order to capture the gradient of properties from the surface towards the substrate, performing progressive indentations, testing in the same location but with increasing depth, starting from 50 and ending at 1000 nm, in steps of ~50 nm. This method allowed a better estimation of both hardness (H) and Young's elastic modulus (E) as it minimizes any indentation size effects. A total number of 10–15 load partial–unload indentations were performed, spaced at ~50 μm. The system calibration was performed using fused silica ($E\approx72$ GPa; $H\approx6.8$ GPa).

viii) Biocompatibility assays: 3T3 cells were used to asses biocompatibility of BG films in terms of adherence, proliferation and cytotoxicity. Dulbecco's Modified Eagle Medium: Nutrient Mixture F-12 (DMEM-F12) cell culture media (with 10% foetal calf serum, 100 UI ml^{-1} penicillin and 100 μg ml^{-1} streptomycin) was used (all materials were purchased from Sigma Aldrich, USA). Cells were maintained at 37 °C in a cell culture incubator with humidified 5% CO_2 atmosphere. Cells were quantified with methyl-tetrazolium salt (MTS) assay according to the manufacturers'

Table 1
Sputtering conditions for the bioglass films.

Sample batch	Working atmosphere	Pressure (Pa)	Total gas flow (sccm)	Power (W)	Target DC_{bias} (V)	Thickness (nm)
BG3	100% Ar	0.3	35	75	~119	~1000
BG4	100% Ar	0.4	35	75	~123	~1000
BG3O1	90% Ar + 10% O_2	0.3	35	75	~96	~1000
BG3O2	80% Ar + 20% O_2	0.3	35	75	~82	~1000