Pulsed Laser Deposition of SiO_2 - P_2O_5 - CaO - MgO Glass Coatings on Titanium Substrates

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Thin films of bioactive glass-ceramic have been deposited on titanium substrates by the Pulsed Laser Deposition (PLD) technique under different experimental conditions. The effect of parameters such as deposition pressure and temperature of heat treatments was studied. The microstructure and the crystalline phases of the coatings were characterized using SEM, EDX and XRD analysis; the phases present were titanium oxides, calcium magnesium silicates and phosphates. The adhesion of the as-deposited films has been examined by scratch tests. The interfacial adhesion of the coatings was better when the deposition was performed at low pressure. Samples were immersed in simulated body fluid (SBF), and a calcium-phosphate precipitate was observed on the surface of less crystallized samples, suggesting that there is some relationship between surface reactivity and crystallinity.

1. Introduction

Many studies have established hydroxyapatite (HAp) as a material of choice for applications involving bone repair and bone-implant contact. On the other hand, new glasses and glass-ceramics based on the SiO_2 - CaO - P_2O_5 system with different amounts of minor constituents exhibit an even greater degree of osteoinductive behaviour[1]. Other advantages of these bioactive glasses include the flexibility inherent to the glass processing methods, and the possibility to manipulate the composition and thermal history in order to adjust the amount and nature of the crystalline phases present in the final material[2,3].

Bioceramics and bioactive glasses are well known for their bioactivity, but their poor mechanical properties constitute a limitation for load-bearing applications. One solution for this problem is to cover metals (such as Ti, Ti alloys, Co - Cr alloys and stainless steel), which form the structural part of the implant, with a ceramic or a vitreous layer[4-6]. The most promising metallic system for implant applications was found to be Ti and its alloys because of their biocompatibility and mechanical properties[7,8].

Plasma-spraying is the most common method used for coating Ti-based implants, because of its simplicity and the ability to form relatively thick layers (typically 50-200 µm) of HAp or glasses[9-11]. However the poor mechanical properties are the major drawback of this kind of coating; the adhesion between the sandblasted titanium surface and the ceramic layer is low because it is almost exclusively due to mechanical interlocking[12]. Alternative techniques such as electrolytic deposition, sol-gel, powder sintering, ion beam deposition, RF sputtering and others have been explored to improve bond strength and other properties of the coatings, but these methods are still very much open to new developments[13,14].

Pulsed laser deposition (PLD) is a technique that is cur-

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rently being applied in a growing number of fields, mainly due to its ability to deposit high quality films from a variety of materials. A unique characteristic of the PLD technique is the production of dense films that preserve the stoichiometry of the target and have a high degree of adhesion to the substrate[15,16]. By controlling the composition of the gas in the vacuum chamber (O_2, Ar and H_2O) and the substrate temperature, both amorphous and crystalline HAp films, α and β tricalcium phosphates and tetracalcium phosphates could be made from the same HAp target[17-19].

In the present study a series of samples were prepared by depositing a bioactive glass on Ti substrates using the PLD technique under different experimental conditions. The effect of parameters such as deposition pressure and temperature of heat treatments was studied. Coatings were characterized in terms of morphology, crystallinity, adhesion strength and *in vitro* behaviour. The relationship between crystallinity and *in vitro* behaviour in SBF is discussed.

2. Experimental

2.1. Deposition and heat treatments

The targets for pulsed laser deposition (PLD) were fabricated by melting and casting a glass with the molar composition 31 SiO_2; 26.7 MgO; 31.7 CaO; 10.6 P_2O_5. This glass, when heated for 1 h at 870 °C, shows the presence of a single Mg-substituted whitlockite phase, $3(Ca,Mg)O.P_2O_5$, but in samples heat-treated at 970 °C enstatite, $(Mg,Ca)O.SiO_2$, also precipitates. This glass-ceramic is machineable and moderately bioactive[20,21]. Commercially available titanium disks (99.6 wt. (%) Ti) were used as substrates. The substrate surface was prepared for deposition by polishing, washing with acetone, immersing in a solution with 15%HNO_3, 1%HF and 84% H_2O (vol%) for 3 min, followed by ultrasonic cleaning in deionised water.

The deposition was performed using a KrF laser (Lambda Physik LPX 300) with a wavelength of 248 nm and a 10 Hz pulse repetition rate. The laser fluence was 5.58 J/cm² and the number of pulses was 18000. The vacuum chamber was always pumped to a base pressure of at least 10^{-7} mbar, and for some depositions the pressure was increased by the introduction of oxygen (10^{-2} mbar). The coatings were deposited at room temperature. The distance between the target and the substrate was fixed at 4 cm. After deposition, some of the coatings were heat-treated for 1h at 870 and 970 °C, in air.

2.2. Characterization

The surface morphology of the films was examined using scanning electron microscopy (Hitachi H9000-NA), and energy dispersive X-ray (EDX) analysis was used for elemental analysis. In order to assess the crystallinity of the as-deposited and heat-treated coatings, X-ray diffraction

(Rigaku PMG-VH) measurements were performed with a scanning speed of 0.1°/min.

The adhesion strength of the coatings was evaluated using scratch tests performed on a CSem-Revetest scratcher with a Rockwell C diamond stylus (hemispherical tip, 200 μm), under linearly increasing load (from 1 to 20 N) with a specimen traversal rate of 10 mm/min. The samples were inspected by SEM and optical microscopy. The adhesion was evaluated by taking into consideration any coating losses, whether by flaking or by massive loss in the scratch channel[22].

In order to test their *in vitro* behaviour in a simulated plasma, the as-deposited coatings and the heat-treated coatings were soaked in 10 mL SBF at 37 °C and pH 7.4 for 7 days, with daily solution renewal. The amounts of Si, Ca, P and Mg ions in solution were analysed by inductive coupled plasma spectrometry (ICP). Morphological characterisation by SEM was carried out before and after SBF immersion.

3. Results and Discussion

### 3.1. Morphology and structure

Figure 1 shows the typical surface morphologies of the coatings as deposited. They consist of a continuous matrix full of spheres ranging in size between 50 nm and 3 μm. This morphology is typical for glass and metal films made by PLD. The spheres are droplets of molten material from the target and they cannot be avoided by manipulating the deposition parameters (temperature, pressure or laser fluence). Even when the substrate is placed off-axis, the glass films made by PLD still present this kind of surface topography[23]. In the films made at low pressure, 10^{-7} mbar (Fig. 1a), the packing of the spheres is very dense, while in the films made at high pressure, 10^{-2} mbar (Fig. 1b), the surface is rougher and the spheres are weakly connected among themselves. The packing density of the spheres is related to the loss of kinetic energy of the particles during the transport of material between the target and the substrate due to the collisions with the O_2 molecules in the chamber atmosphere.

The coatings had thicknesses ranging between 1 and 5 μm, but it was not easy to have an exact measurement because of the roughness of the substrate, the morphology of the coatings and the difficulty in fracturing the titanium substrates without destroying the coatings. In order to observe the cross sections of the films, some coatings were repeated on silicon substrates using the same experimental conditions. Fig. 2 shows the cross section of one of the coatings made at low pressure (10^{-7} mbar). The film is very compact and the spheres are closely packed forming a dense matrix. The thickness of this film is approximately 4 μm. In this picture one can have a better idea about the size of the

droplets of molten glass in relation to the thickness of the film. For this particular application the surface roughness due to the spheres is actually favourable because it helps the osteointegration of the implants[24].

Figure 3 shows the XRD patterns of the titanium substrates heat-treated at 870 °C and 970 °C, for 1 h in air, and substrates with coatings prepared at 10^{-7} mbar and heat-treated at the same temperatures. The heat-treated coatings are crystallized even for the lower heat treatment temperature and exhibit peaks from titanium oxides, as well as peaks that can be attributed to calcium magnesium phosphates and calcium magnesium silicates, whereas the diffractograms for the heat-treated substrates show only the peaks characteristic of Ti$_3$O and TiO$_2$. With the increase of the heat treat-

ment temperature the peak intensities increase, indicating a higher degree of crystallinity in the films, and a series of small peaks appear at low diffraction angles, all of them

Figure 2. Cross section of a film made at low pressure (10^{-7}mbar) on a silicon substrate.
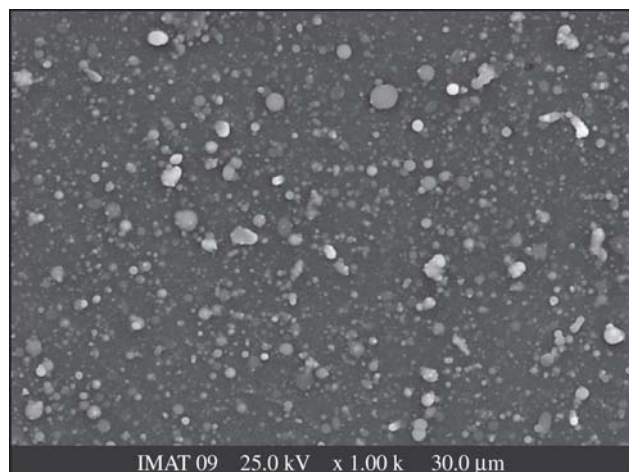
(a)
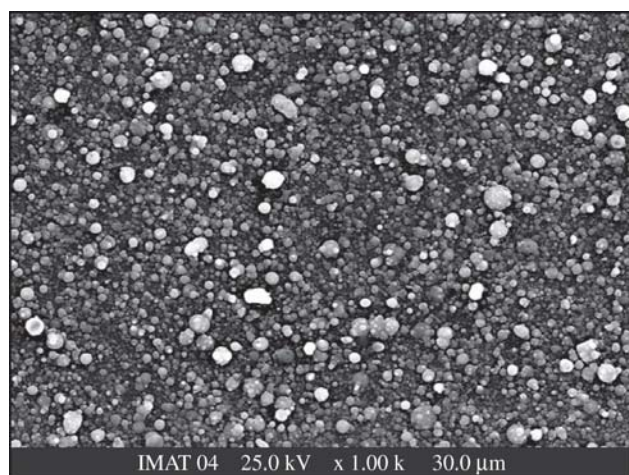
(b)

Figure 1. SEM micrographs of typical film surfaces made at: a) low pressure (10^{-7} mbar); b) high pressure (10^{-2} mbar).
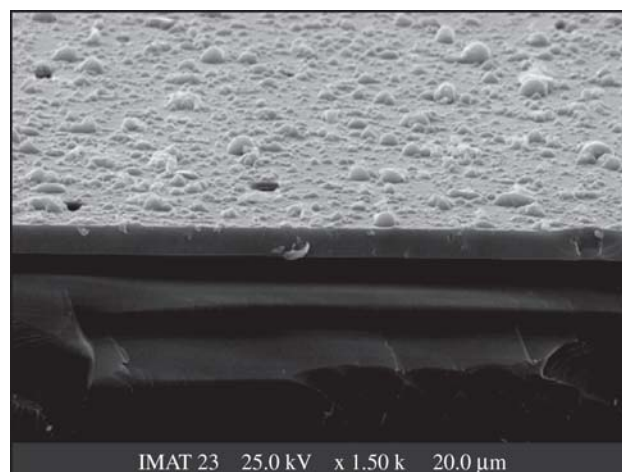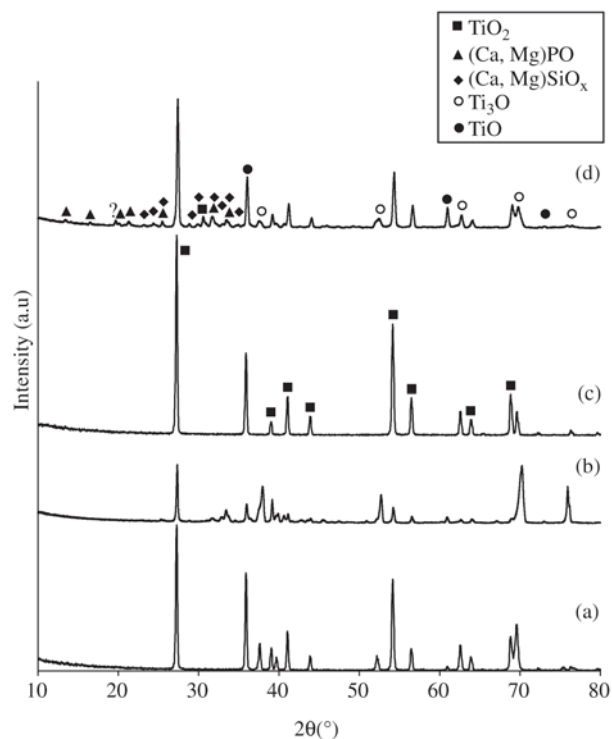

Figure 3. X-ray diffraction patterns of samples heat-treated for 1 h in air: a) Titanium, 870°C; b) Coated titanium, 870 °C; c) Titanium, 970 °C; d) Coated titanium, 970 °C.

corresponding also to the phosphates and silicates with the exception of one peak which could not be identified. These peaks are not present in the diffractogram for the Ti substrates heat-treated under the same conditions. Previous DTA studies on samples from the same glass showed two exothermic peaks at 829 °C and 936 °C, corresponding to the onset of crystallization for these two phases[25].

The morphology of the heat-treated coatings is shown in Figs. 4a and 4b. In the case of the heat treatment at 870 °C, the coatings appeared to begin their crystallization, while at 970 °C an extensive oxidation of the metallic substrate occurred and two different morphologies, thin plates and agglomerates were observed. The EDS analysis showed that the agglomerates in the sample heat-treated at 870 °C are richer in Ca and Mg than the surrounding matrix. In the sample heated at 970 °C, the molar concentration of Ti in the plates is higher than the concentration of Ca and Mg, whereas the opposite happens in the agglomerates.

3.2. Adhesion

The inherent properties of the coating and the substrate, namely the coating morphology and the substrate surface roughness, make the measurement of the adhesion strength very difficult. Due to these characteristics, the scratch test does not give reliable information of the load that is representative of the coating adhesion; it can only provide qualitative results, useful for comparative studies.

The interfacial adhesion of the glass coatings is better for the lower deposition pressure (10^{-7} mbar), than for the higher deposition pressure (10^{-2} mbar) as observed in Fig. 5a and 5b, respectively. This was expected from the surface morphology of the films shown in Fig. 1. The films made at low pressure are denser while in the films made at high pressure the cohesion between the glass spheres is weaker and as a result a lower adhesion was obtained.

3.3. Surface reactivity in SBF

After soaking in SBF, the as-deposited coatings made at low pressure showed signs of surface dissolution (Fig. 6a). This type of behaviour was also observed by Wolke *et al.*[26] for amorphous calcium phosphate coatings (4 μm thick) deposited by RF magnetron sputtering, but the authors reported a good durability for much thinner (0.1μm thick) heat-treated coatings even after 4 weeks immersion in SBF. Although the coatings deposited by PLD and sputtering are thinner than the ones made by plasma spraying, they are denser, more homogeneous and more adherent, consequently having improved mechanical properties[18,26,27]. For the coatings heat-treated for 1 h at 870 °C a granular precipitate was deposited (Fig. 6b). EDS analysis showed that this precipitate was rich in Ca and P. In the case of the coatings heat-treated for 1h at 970°C no changes were observed.

The growth of the Ca-P precipitate was only observed on the coatings heat-treated for 1 h at 870 °C. As shown in Fig. 3, the samples heat-treated at 870 °C are less crystallised than the ones at 970 °C. It is likely that calcium phosphate nuclei formed in SBF grow faster on samples with a residual glassy phase, since super saturation of the SBF solution will be favoured by dissolution of the glass matrix. The presence of a certain amount of amorphous phase is thought to be essential in promoting dissolution of the material and further growth of the apatite layer in a simulated
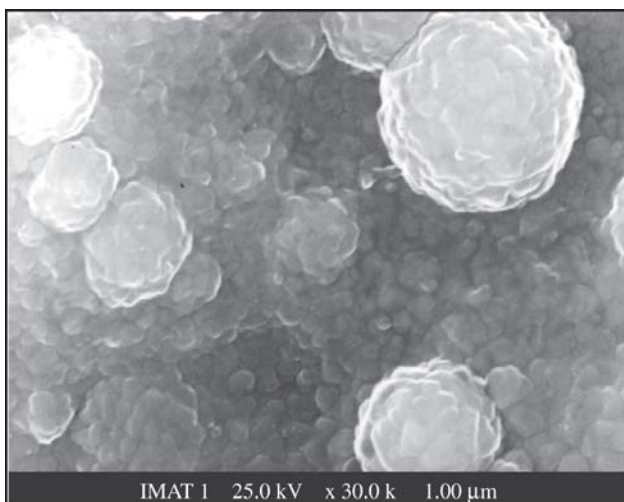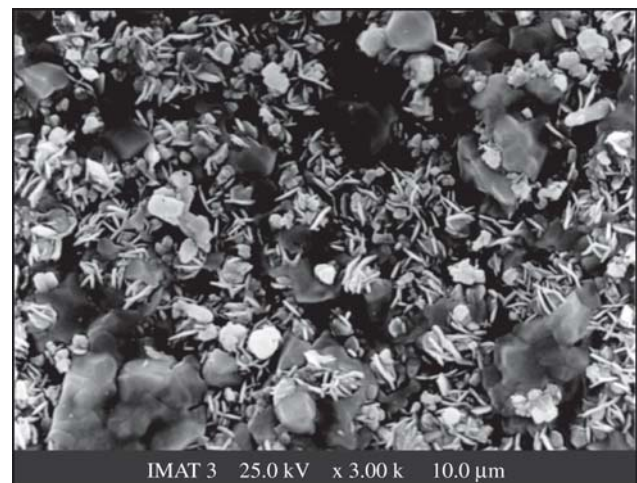
(a)   (b)

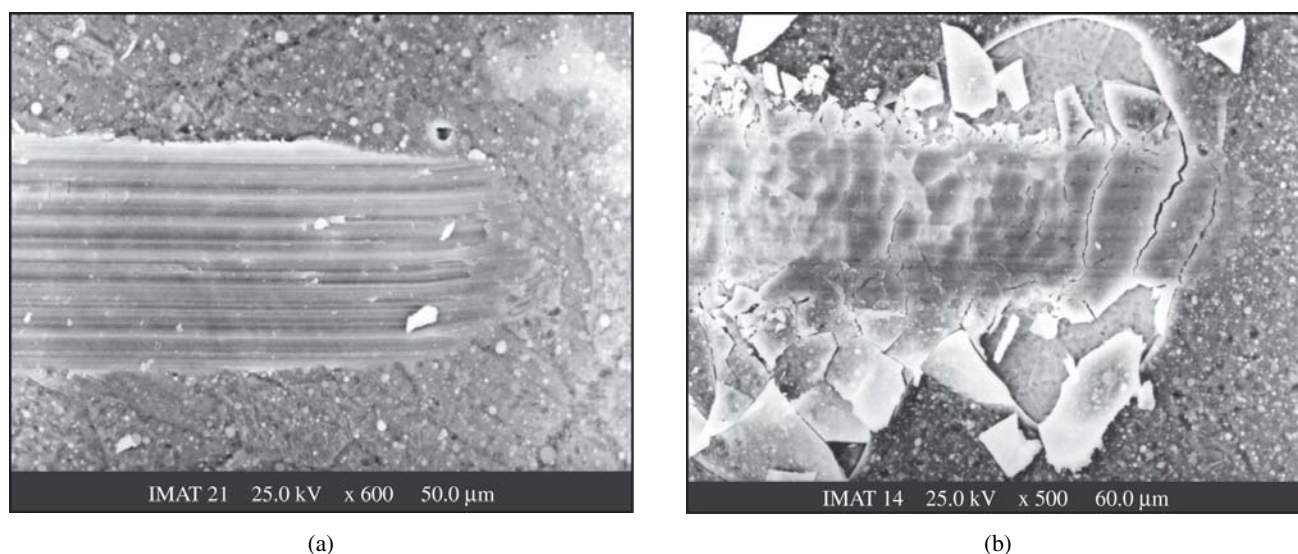**Figure 4.** Scanning electron micrographs of heat-treated coatings: a) 870 °C, 1h; b) 970 °C, 1 h.

(a)

(b)

Figure 5. SEM picture of a scratch test performed on as-deposited coatings grown at: a) low pressure (10^{-7} mbar); b) high pressure (10^{-2} mbar).
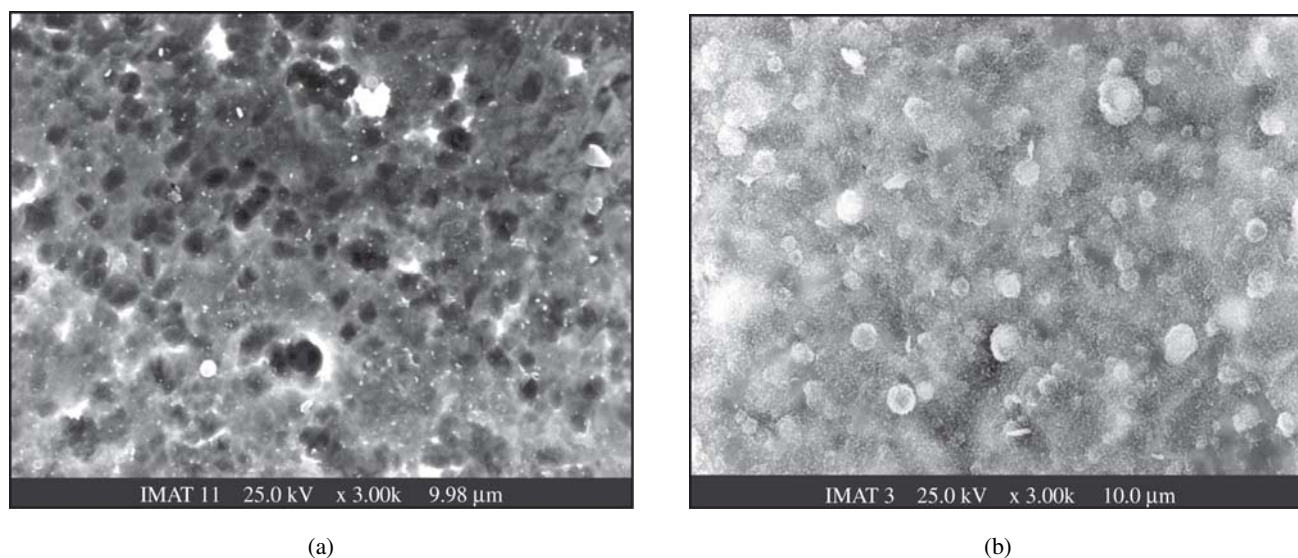

(a)

(b)

Figure 6. SEM micrograph of coating surface after 7 days in SBF with renewal: a) as-deposited coating; b) heat-treated coating at 870 °C.

plasma[26,28]. In the case of the coatings heat-treated at 970 °C, the Ca-P precipitate did not appear after immersion in SBF probably because the coatings were almost fully crystallised, as suggested by Figs. 3d and 4b.

The elemental concentrations of Si, Ca, P and Mg, obtained by ICP confirmed that dissolution in SBF of the as-deposited coatings was more severe than in the samples heat-treated in both conditions, as shown in Table 1. In contrast with the as-deposited coatings, the heat-treated coatings dissolved only slightly; after the test, the Ca and P concen-

trations in solution were similar to the original ion concentration in the SBF.

4. Conclusions

Adherent coatings of a glass with composition 31 SiO$_2$; 26.7 MgO; 31.7 CaO; 10.6 P$_2$O$_5$ (mol %), previously identified as potentially bioactive, were obtained by pulsed laser deposition on Ti substrates. All the as-deposited coatings exhibited an amorphous structure. The crystallinity of the coatings was promoted by post-deposition heat treat-

Table 1. Elemental concentration of the SBF after immersion of coatings.

Heat Treatment	Elemental Concentrations (mg/l)			
	P	Mg	Ca	Si
–	33.0	37.4	106	8.63
870 °C,1 h	30.3	34.8	97.6	< 0.5
970 °C,1 h	31.1	35.0	98.1	< 0.5
SBF	29.9	33.7	96.9	< 0.5

ments. Titanium oxides, calcium magnesium silicates and phosphates were present in the heat-treated coatings. Scratch tests provided indication that the interfacial adhesion of the coatings was better when the deposition was performed at low pressure.

The coatings heat-treated for 1 h at 870 °C induced the formation of a Ca - P precipitate when immersed in a renewed SBF solution; this did not occur for the amorphous coatings and for the coatings heat-treated at 970 °C for 1 h in air. These results suggest that, similarly to what happens with bulk bioactive glasses and glass-ceramics, the behaviour of the coatings in simulated plasma is dependent on the amount of glassy phase present. Work is now in progress to clarify the mechanisms of apatite formation on the surface of the coatings and to confirm if the *in vitro* bioactivity observed in bulk samples is maintained in the films deposited by the PLD technique.

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