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SYNTHESIS AND CHARACTERIZATION OF BIOGLASS THIN FILMS

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We report the successful pulsed laser deposition on medical grade Ti substrates of thin films made of two bioactive glasses in the $SiO_2 - Na_2O - K_2O - CaO - MgO - P_2O_5$ system. The films were topographically and chemically characterized by confocal scanning laser microscopy and Fourier transform infrared spectrophotometry. Our studies proved that chemical composition was similar in the base material and deposited films. The latter were rather uniform and rough enough to favor enhanced biocompatibility

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1. Introduction

The use of bioactive glasses to make prosthetic implants has revolutionized the biomedical field. Many implant materials made of glasses have been used for the past three decades. As part of efforts to improve the biocompatibility and mechanical strength of implant materials, attention has been drawn by the potential of glass-glass composites. Glass-based biomaterials have been accepted after biological evaluation by several in vivo and in vitro tests.

Bioactive materials elicit a specific biological response at the interface of the material leading to the formation of a natural bond (first demonstrated in 1969) [1] and development of new mineralized bone tissue. Materials in this class include dense calcium phosphate ceramics, bioactive glasses (45S5 Bioglass®), bioactive glass-ceramics (Cerevital®, Wollastonite A/W glass-ceramics, machinable glass-ceramics), bioactive composites (Palavital®, stainless steel-fiber reinforced Bioglass®), and polyethylene- HA mixtures, etc. [2].

Because of biomechanical limitations, bioglasses, glass-ceramics, and calcium phosphate ceramics are mainly used in low or non-bearing applications [3]. For obvious reasons, metals are mechanically suitable for load-bearing orthopedic and dental implants. Nevertheless, various difficulties related to corrosion, wear, and negative tissue interactions have been reported [4]. Coating metallic implants with thin layers of bioactive material combines mechanical advantages with excellent biocompatibility. Furthermore, the coatings can protect the implants from corrosion, limiting the release of metallic ions into the body [5-8]. For chemically binding coating (orthopedic, dental, or maxillofacial prosthetics), hydroxylapatite, bioactive glasses and bioactive-glass ceramic layers have been applied.

Pulsed laser deposition (PLD) has emerged as a successful technique for growing high-quality crystalline and stoichiometric thin films [9-15]. Moreover, PLD has the unique ability of creating a wide range of coatings with very different, even opposite attributes, e.g., amorphous/crystalline, smooth/dense, and rough/porous [16]. The technique is often used to produce mono- and multilayer thin structures made of materials or combinations of materials that would be very hard to process by other methods. PLD's main edge is its capability to transfer complicated material compositions to a substrate without changing their stoichiometry, a phenomenon usually described as congruent ablation and deposition.

We herewith report an extension of PLD to make bioactive coatings using a new family of glasses in the $SiO_2 - Na_2O - K_2O - CaO - MgO - P_2O_5$ system, developed by Tomsia at al. [17,18]. We used a medical grade, chemically etched, Ti substrate because titanium is the most popular choice for the fabrication of

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orthopedic implants where high strength is required. In addition, the depositions were characterized from both the compositional and morphological points of view.

2. Materials and methods

We used two types of glasses, 6P57 and 6P61 (Table 1), belonging to the earlier mentioned system. The glasses were prepared by a conventional procedure that involved mixing adequate amounts of SiO_2 (99%, Kemika, Cro), $CaCO_3$ (pa, Kemika, Cro), $MgCO_3$ (pa, Kemika, Cro), Na_2CO_3 (99%, Sinex, Srb), K_2CO_3 (99%, Zorka, Srb), and NaH_2PO_4 (99%, Riedel-de Haën, Ger) powders [19]. The appropriate reagents were mixed and the mixture was subsequently melted, broken up, fritted, grinded, and filtered. The obtained powder was pressed using a Specac mould, 13 mm in diameter, and then sintered at 650 C.

The result was a hard compact pellet having the same diameter as the cast and 2 mm thickness, as determined by the amount of material used.

Table 1. Compositions (in wt %) and thermal expansion coefficient of bioglasses used in the preparation of PLD coatings. Thermal expansion coefficient of Ti in substrates

	SiO_2	Na_2O	K_2O	CaO	MgO	P_2O_5	$\alpha(K^{-1})$
Titanium							$9.2\ 10^{-6}$
6P57	56.5	11.0	3.0	15.0	8.5	6.0	$10.8\ 10^{-6}$
6P61	61.1	10.3	2.8	12.6	7.2	6.0	$10.2\ 10^{-6}$

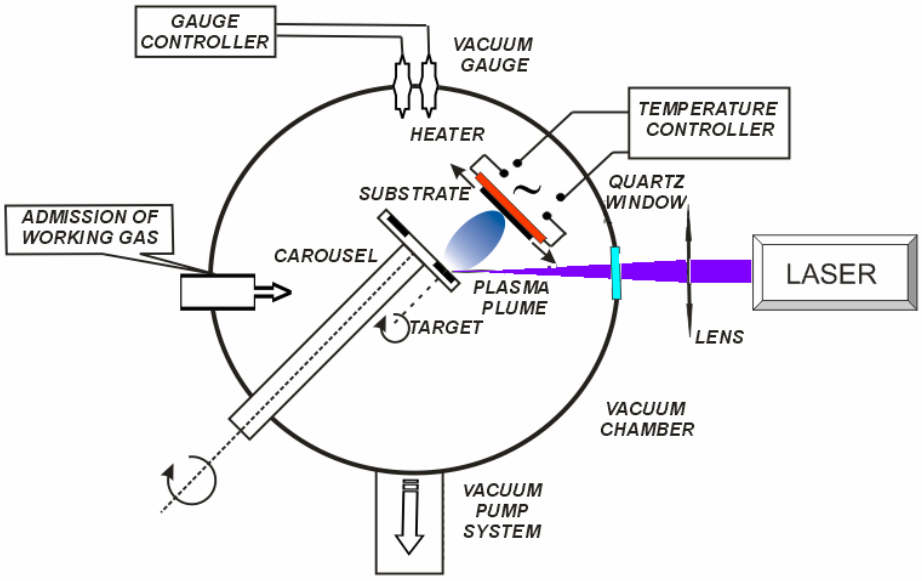


Fig.1. General schematic of the PLD setup used in experiments

Such pellets served as targets in PLD experiments (Fig.1). Material ablated from the target under laser irradiation was collected onto a nearby Ti substrate and a bioglass thin film was deposited.

A KrF* excimer laser source ($\lambda = 248\,\text{nm}$, $\tau_{FWHM} \sim 25\text{ns}$) was used for deposition. It was operated at 400 mJ per pulse, while incident fluence on target surface was varied within the range (4-8) J/cm^2. The films were grown in low pressure (13 Pa) oxygen on Ti grade 4 (99.6%) substrate chemically etched. The chamber was evacuated down to a residual pressure of 10^{-4} Pa prior to every deposition. During deposition, the substrates were held at a constant temperature of 400°C. The target-substrate distance was 4 cm. For the deposition of each film, we applied 5000 subsequent laser pulses at 10 Hz repetition rate. To avoid drilling, the target was rotated with a frequency of 0.4 Hz during multipulse irradiation, while to improve films morphology, some translations were performed along two orthogonal directions.

FTIR investigations were performed with a Perkin Elmer BX II with high intensity ceramic light source. We used a Ge-coated KBr beam splitter and a Peltier thermostated DLATGS detector. The wavenumber range 7800 - 350 cm^{-1}, spectral resolution 0.4 cm^{-1}, S/N ratio 20000:1. The spectra were taken in the reflectance mode.

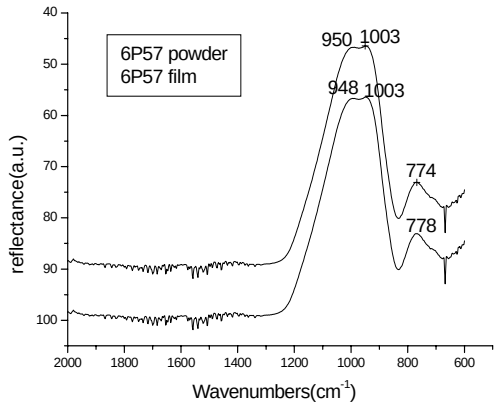
The deposited structures were analyzed by confocal scanning laser microscopy (CSLM) and Fourier transform infrared spectrophotometry (FTIR). The roughness and topography of the bioglass surface were investigated by CSLM.

The CSLM investigation process is based upon sequential exploration of samples by a laser beam and acquisition of resulting interaction effects between light and material for surface or spatial imaging. For nondestructive investigation of specimens by CSLM we used a Leica TCS SP system equipped with a He-Ne laser emitting at 633nm wavelength and a set of PL Fluotar (10X, 40X, numerical aperture NA 0.7) objectives. The images were obtained in reflection mode. Data processing and displaying were made by Leica software designed for an independent Graphic Station.

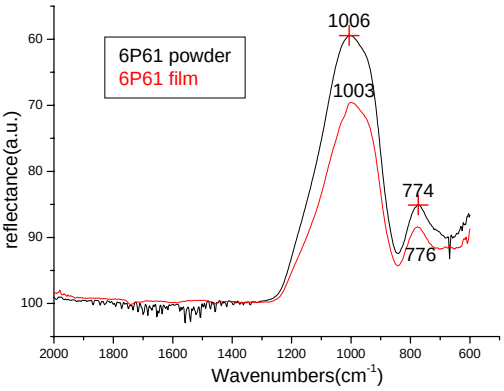
3. Results and discussion

Our investigations have shown that the best compromise between structural fidelity and uniformity of bioglass thin films deposited on titanium was obtained for 5.5-6 J/cm^2. Most of our studies were therefore performed with an incident laser fluence of 5.7 J/cm^2.

FTIR analyses revealed the presence of SiO_2 molecular bindings in powder, pellet, and obtained films, and the absence of any supplementary peaks due to impurities (Fig. 2). These features make a strong case for PLD's preservation of the chemical composition of the base material in this case.



a)



b)

Fig.2. FTIR spectra of both powder and deposited film for: a) 6P57 and b) 6P61 bioglasses

Topographic analyses by CSLM showed the layers obtained by PLD were uniform and copied the titanium substrate microrelief (Figs. 3-6).

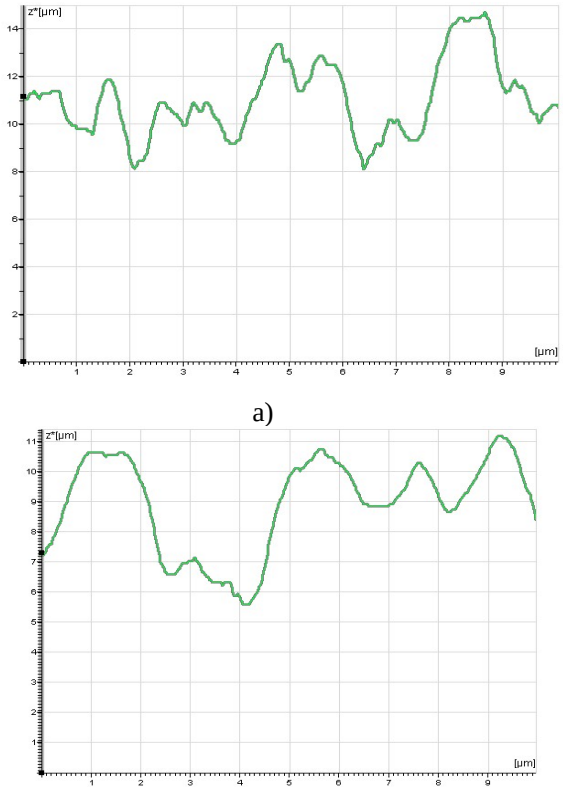


Fig. 3. Surface profile along a random 10 µm length zone in the cases of a) 6P57 and b) 6P61 bioglass films on Ti substrates.

In Fig.3, for example, one notices a maximum amplitude of the surface profile variation of 15 µm and a minimum one of 8.25 µm in the case of the 6P57 bioglass film (Fig. 3a). Slightly lower values of 11.40 µm and 5.70 µm, respectively, were found for the 6P61 bioglass film (Fig. 3b).

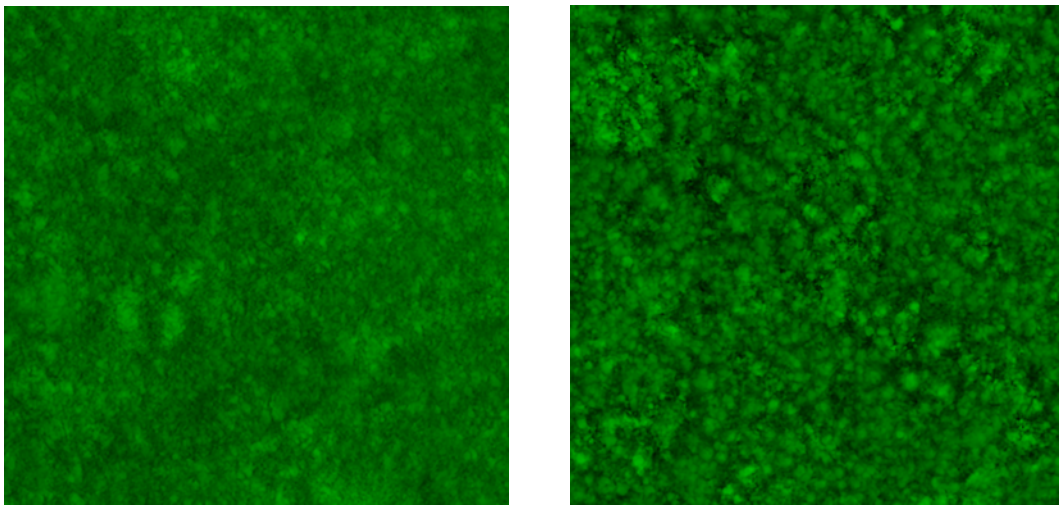
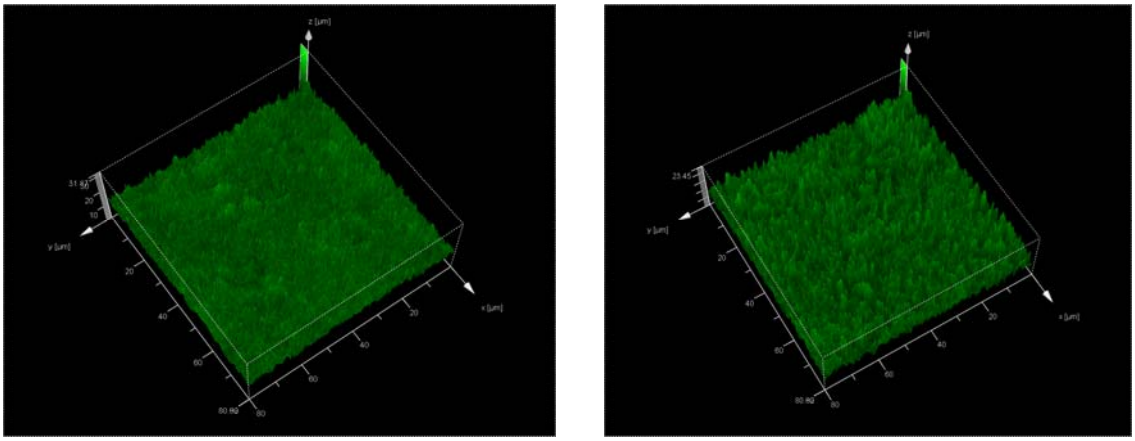


Fig. 4. Surface topography, zoom 1, 10 X magnification, for a) 6P57 and b) 6P61 bioglass films.

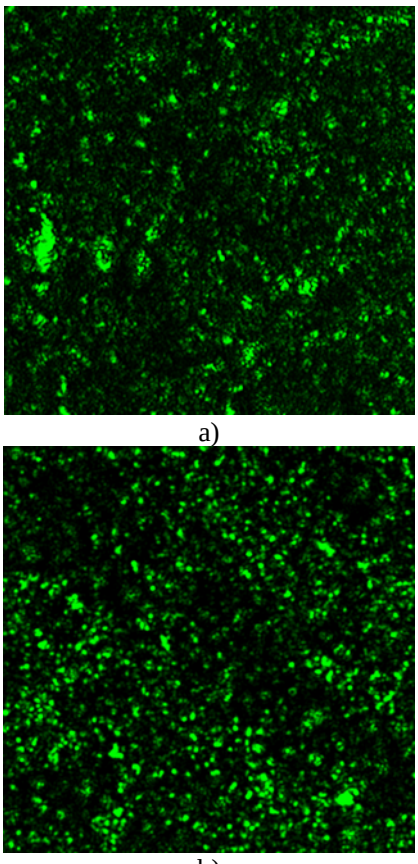
3D images of the deposited thin films (fig.6) revealed the formation of a structure with a special configuration, consisting of a great number of protuberances of 20-30 μm maximum height. Such feature favors biocompatibility which significantly increases with the specific area of the deposited biofilms. Indeed, the rougher the area due to surface protuberances, the higher the proliferation of viable cell cultures.



a) b)

Fig. 5. CLSM 3D image, zoom 3.12, 40X magnification, for a) 6P57 and b) 6P61 glass films.

We processed the images in Fig. 6 with a dedicated software, which enabled us to infer a 300-350 nm size of the particulates present on surface and about 150 nm mean surface roughness of both 6P57 and 6P61 bioglass films.



a)

b)

Fig. 6. CLSM 2D image, zoom 3.12, 40X magnification, for a) 6P57 and b) 6P61 glass films.

Next, by statistically exploring the spatial characteristics of the 3D surface contours from the z-heights in Fig. 5, we obtained the histograms in Fig.7. The histogram is a Gaussian distribution further supporting surface uniformity.

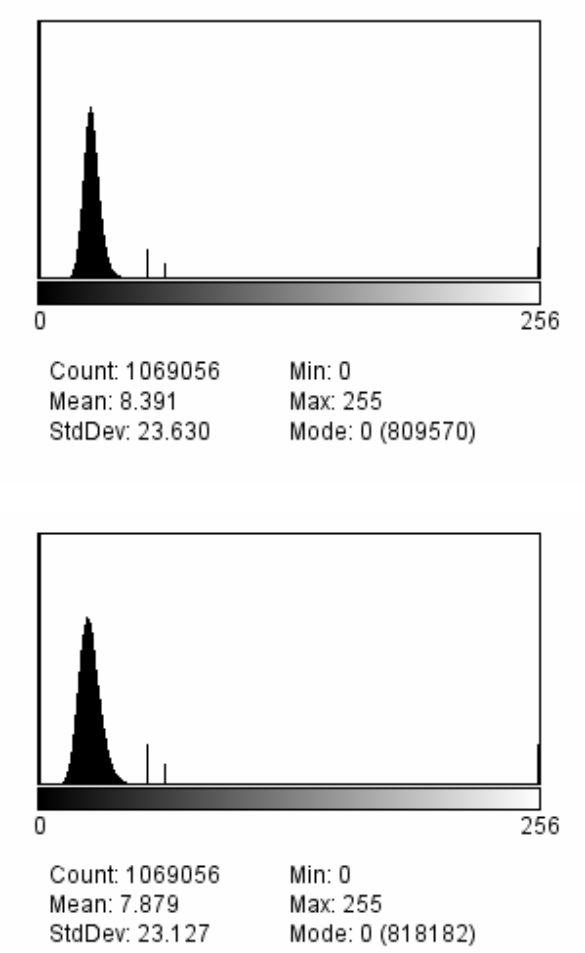


Fig.7. Histograms on 1mm x 1mm area, 10X magnification, for a) 6P57 and b) 6P61 bioglass thin films.

4. Conclusion

We have deposited uniform thin films by PLD in low pressure oxygen from bioglasses with different SiO_2 content, of 56.5 wt % and 61.1 wt %, respectively. We demonstrated by FTIR that PLD transfer was stoichiometric and proved by CSLM the smoothness of the obtained structures, which copied the topography of their chemically etched Ti substrates.

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