# ADHERENT GLASS-CERAMIC THIN LAYERS WITH BIOACTIVE POTENTIAL DEPOSITED BY MAGNETRON SPUTTERING TECHNIQUES

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*Filme subțiri de biosticlă au fost preparate pe substraturi de titan prin tehnologii de pulverizare în plasmă magnetron în regim de radio-frecvență, folosind ca țintă catod o pulbere de biosticlă silicatică tip 45S5 Bioglass®. Două presiuni de lucru au fost utilizate: 0,16 Pa şi respectiv 0,45 Pa. Structurile preparate au fost apoi investigate din punct de vedere morfologic, compozițional şi structural prin FTIR şi SEM-EDS. Cele mai bune rezultate din punctul de vedere al stoichiometriei transferului țintă-substrat şi a compoziției chimice au fost obținute în cazul presiunii mai mari. Pentru această presiune, efectul tratamentului termic la 700°C/2h a fost studiat în continuare pe două tipuri de structuri: abrupte şi cu strat tampon cu gradient de compoziție. Caracterizările SEM au evidențiat o morfologie mai bună fără fisuri sau exfolieri în cazul structurilor „gradate".*

*Bioglass coatings were prepared by RF magnetron sputtering techniques onto titanium substrates from a 45S5 Bioglass® powder target. Two working pressures were used: 0.16 Pa and respectively 0.45 Pa. The structures were investigated from morphological, compositional and structural point of view by FTIR and SEM-EDS. The best results in terms of target-substrate stoichiometric transfer and chemical composition were obtained for the higher argon pressure. In case of this pressure, the effect of heat-treatment in air at 700°C/2h was further studied upon two types of structures: abrupt and with functional graded buffer layer. SEM characterizations revealed a better morphology without cracks or delaminations for the "graded" structures.*

**Keywords:** bioglass coatings, magnetron sputtering, FTIR spectroscopy, SEM-EDS, functional graded materials

## 1. Introduction

Titanium and some of its alloys are successful biocompatible materials extensively used for biomedical applications, especially for bone-replacement systems, such as dental and orthopedic implants. These materials possess good bulk mechanical properties such as a low modulus of elasticity, a high strength-to weight ratio, excellent corrosion resistance and biocompatibility which are

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enhanced by an inert surface oxide film grown by passivation [1, 2]. Despite the already good biocompatibility of these materials there is a need for further improvement because of a slower healing process and respectively of the increasing life expectancy, which results in a prolonged retention period of such medical devices in the human body.

One successful approach for enhancing the biocompatibility of the titanium based medical devices is the coating with biologically active materials such as calcium phosphates or bioglasses.

The first bioglass (BG) known as 45S5 Bioglass® (45 $SiO_2$, 24.5 CaO, 6 $P_2O_5$ and 24.5 $Na_2O$ wt %) was reported in 1968 [3, 4]. The silica-based biological glasses present unique bioactive properties, capable of activating and enhancing the osteosynthesis process, and creating a direct connection with bone tissue through chemical bonds. This takes place for a $SiO_2$ content smaller than ~60 wt %, high $Na_2O$ and CaO content and a high Ca/P ratio (between 1÷5) [3]. The glass-ceramics structures were intensively used in the last four decades as bone grafts or osseous fillers for local defects in orthopedic and dental surgery. Unfortunately the coating of titanium substrates with thick BG films by enameling and plasma spray techniques, usually fail due to a weak glass/metal interface and rapid dissolution in body fluids when implanted [5-7].

Radio-frequency magnetron sputtering (RF-MS) represents a flexible technique for preparing a various range of materials as coatings on metallic substrates. This technique facilitates the producing of dense and well-adhered films with controlled elemental composition [8]. Examples include hard, wear-resistant coatings, low friction coatings, corrosion resistant coatings, decorative coatings and coatings with specific optical or electrical properties.

The aim of this work was to synthesize bioglass coatings on Ti substrates with good stoichiometry and high adherence properties. We investigate in comparison the magnetron (co)-sputtering technique as a possible alternative method for producing high quality coatings via the introduction of a buffer layer $BG_{1-x}Ti_x$ (x=0÷1) with chemical gradient of composition. Such structures could allow combining the good mechanical properties of the metals or alloys with the bioactive surfaces conferred by the glass material.

## 2. Materials and Methods

### *2.1 Materials*

Commercially pure titanium (Mateck GmbH, cp-Ti gr. 1) and glass substrates (Corning 1737) were used as substrates. All substrates were ultrasonically cleaned in acetone and iso-propanol before deposition. The magnetron sputtering BG target (110 mm diameter, 3 mm thick) was prepared by cold-pressing from a 45S5 silica-based bioactive glass powder with ~ 7.5 micron granular size. An additional solid target of pure titanium was used for co-sputtering depositions.

*2.2 Principle and magnetron sputtering deposition technique*

In the planar magnetron cathode geometry a typical DC electric field of ~ 100 V/cm is impressed between the cathode target and anode (substrate). Small permanent magnets are arranged on the back of the target in either ellipse-like or circular rings depending on whether the targets are rectangular or circular in shape. A magnetic field is created by these permanent magnets. Roughly half of the total magnetic field (B) distribution emerges from the north pole roughly perpendicular to the front target face into the inter-electrode space. Then the field lines arch over with a portion parallel to the target surface. Finally B returns roughly normal to the target surface into the south pole, completing the closure of field lines. Electrons launched slightly off the target normal will initially spiral along the B field lines emanating normal to the target. In the region where the electric (E) and magnetic (B) fields are perpendicular to one another, electrons are forced to drift in a cycloidal hopping motion along the tunnel track length. This configuration acts to trap electrons. Thus, in a magnetron sputtering discharge, atoms are sputtered from the cathode target by magnetically confined plasma.

The target material is sputtered by the bombardment of high energy ions accelerated over the cathode sheath potential. Secondary electrons are emitted and accelerated away from the target surface as a result of the ion bombardment. These electrons play an important role in maintaining the plasma. A magnetic field confines the ionizing energetic electrons near the cathode allowing operation at high plasma densities and low pressures. This method is quite successful in producing high-quality, low-impurity films at reasonable deposition rates [9].

*2.3 Deposition of bioglass layers*

A UVN-75R1 sputtering system equipped with two planar magnetron cathodes was used. In the first step, the work chamber was evacuated with a diffusion pump, which was backed by a mechanical pump, to a base pressure lower than $10^{-3}$ Pa. Ultra-high purity argon was used as sputtering gas. Prior deposition, the substrates were etched for 10 min at a 0.4 kV $DC_{bias}$ voltage in argon plasma beneath a wolfram plasmatron. Pre-sputtering of the BG and Ti targets was performed when they were first pumped down, in order to activate their surface. During this phase surface contaminants were removed and deposited onto an externally shutter placed between the targets and the substrates.

Low RF power (~100 watts) was applied to the cathode targets, with the substrate holder positioned at a 30 mm distance in front of them. Two working pressure were used: 0.16 Pa (sample indicative – BG-1) and 0.45 Pa (sample indicative – BG-2) in order to investigate the pressure influence over the deposition rate, and respectively stoichiometric target-substrate transfer.

The BG/Ti "abrupt" coatings were prepared by RF magnetron sputtering from the BG target. The depositions were carried out for 1 h, using a 1.78 MHz generator at a constant and $DC_{bias}$ target value of 45V.

The "graded" $BG/BG_{1-x}Ti_x/Ti$ ($x=0\div1$) structures were prepared by co-sputtering, slowly moving the rotating substrate holder from the Ti target towards the BG one. By this procedure a functionally graded transition zone with variable chemical composition can be formed between the top biofunctional coating and the titanium substrate. This process took 5 minutes, the graded layer thickness being estimated at around ~ 70 nm. Finally the described functional graded structures were kept for 1 hour in front of the BG target, in order to prepare the biofunctional BG HA layer.

During the sputtering process the temperature of the substrates reached around 150ºC due to heating from the plasma discharge as monitored with a Cromel-Alumel thermocouple system. The BG deposition rate was estimated using the Swanepoel procedure [10] from optical spectroscopy transmission data, in case of films deposited in identical conditions onto Corning glass substrates.

After deposition, one series was left as-sputtered for comparison studies, while the other series was annealed in air at 700°C for 2 hours with a low cooling rate (3°C/min) in order to induce a phase transition from the amorphous to the crystalline one, and study the morphological changes.

### *2.4 Morphological, structural and compositional characterizations*

The BG samples were gold coated in an ion sputter system and examined for their surface topography and morphology in scanning electron microscopy (SEM, model JEOL 35 MT 330) operating at an accelerating voltage of 20 kV. A chemical compositional analysis was performed by energy dispersive spectrometry (EDS, model Rontec Edwin WinTools), in order to evidence the stoichiometry of the target-substrate transfer in magnetron sputtering technique.

For evidencing the molecular vibration modes of the chemical bonds or functional groups present in the bioglass structure FTIR experiments were performed using a Perkin Elmer BX Spectrum-Pike spectrometer. The spectra were collected in ATR mode in the range 4000 - 400 $cm^{-1}$, with a resolution of 4 $cm^{-1}$ using a Pike-MIRacle diamond head (1.8 mm diameter). The optical measurements of the BG thin film deposited on glass substrates were carried out at room temperature using Perkin-Elmer UV-VIS-NIR Lambda 90 spectrophotometer in the wavelength range from 200 to 800 nm.

## 3. Results and Discussions

### *3.1 Sputtering rate determination*

The dispersive refractive index $n$ and thickness $d$ of thin films were determined from measurements of both transmission and wavelength values by Swanepoel's envelope method [10]. The excellent surface quality and homogeneity of the film were confirmed from the appearance of interference fringes in the transmission spectra. A 1.7 refractive index $n_{BG}$ at different wavelengths was calculated using the envelope curve for $T_{max}$ and $T_{min}$ in the transmission spectra, considering the refractive index of the substrate $n_s$ =1.52. The thickness of the BG thin film was then determined from interference fringes of transmission data measured over the visible range (Table 1).

*Table 1*

**Deposition pressure vs. sputtering rate**

| Sample | Pressure (Pa) | Deposition time (min) | Thickness (nm) |
|---|---|---|---|
| ***BG1*** | 0.16 | 60 | 1020 |
| ***BG2*** | 0.45 | 60 | 420 |

One can notice that the thickness of the BG films decreased with the increase of work pressure. When the working pressure was increased from 0.16 Pa to 0.45 Pa, the mean free path of the sputtered particles decreased. On increasing the sputtering pressure, during traveling from the target to substrate, the sputtered particles suffer more collisions, and some of the sputtered particles are back scattered towards the target. This resulted in a decrease of the deposition rate due to the scattering processes.

### *3.2 EDS compositional analysis of target powder and as-deposited coatings*

The EDS results reveal a quasi-stoichiometric transfer for Si and P, while the concentration strongly increase for Na, and decreases for Ca. One can notice a monotonous enrichment in Si and Ca, and a monotonically depletion in Na and P with the increase of working pressure (Table 2). The most stoichiometric transfer and the better Ca/P molar ratio (~ 2.69) were obtained for the BG2 films (Tables 2 & 3). Obtaining suitable stoichiometric target-substrates atomic transfer was one of our objectives. Thus, taking into account the overall composition of the films vs. the working pressure (Table 3) we can conclude that the most promising layer was obtained at the highest working pressure (0.45 Pa). Based on previous studies one can presume a better bioactive behavior for the BG2 composition [3, 4].

*Table 2*

**Chemical composition in at% and Ca/P molar ratios of the BG target powder and of the as deposited films**

| Sample/Content | Si | Ca | P | Na | Ca/P |
|---|---|---|---|---|---|
| **Target 45S5 (at%)** | 36.35 | 21.19 | 4.1 | 38.35 | ~ 5 |
| **BG1 (0.16 Pa)** | 35.02 | 8.51 | 6.31 | 50.16 | ~ 1.34 |
| **BG2 (0.45 Pa)** | 36.15 | 14.78 | 5.49 | 43.58 | ~ 2.69 |

*Table 3*

**Chemical composition in oxides of the BG target powder and of the as deposited films**

| Sample/Content | $SiO_2$ | CaO | $P_2O_5$ | $Na_2O$ |
|---|---|---|---|---|
| **Target 45S5 (wt%)** | 45 | 24.5 | 6 | 24.5 |
| **BG1 (0.16 Pa)** | 45.91 | 10.41 | 9.77 | 33.91 |
| **BG2 (0.45 Pa)** | 45.83 | 17.48 | 8.21 | 28.48 |

The effect of annealing for crystallization was studied further on BG2 coatings. We investigated in comparison BG2/Ti abrupt coating produced by sputtering and respectively $BG2/BG_{1-x}Ti_x/Ti$ (x=0÷1) graded structures prepared by magnetron (co)-sputtering technique. A partial crystallization of the BG films is preferred in order to reduce the dissolution rate in body fluids. A total crystallization of the BG suppresses its bioactivity [11].

### *3.3 FTIR measurements*

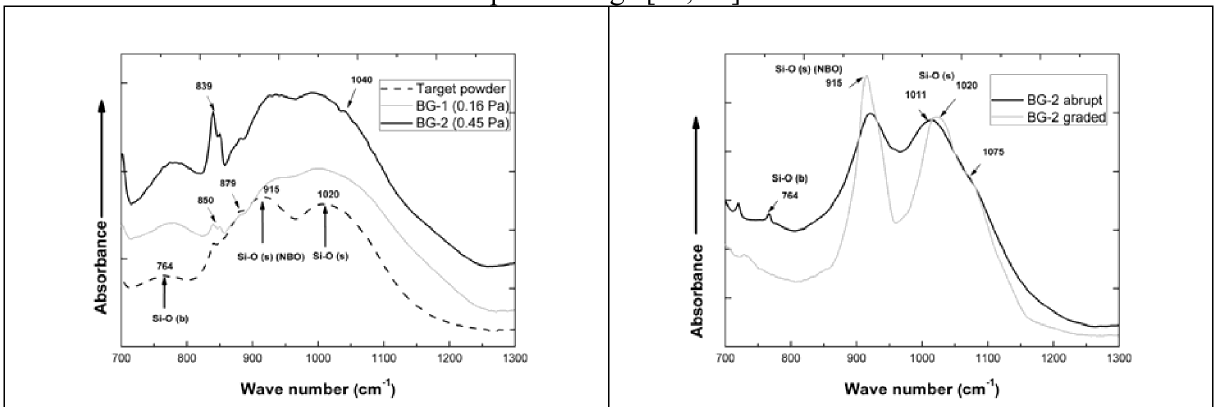
FTIR investigations in, reflection mode, evidenced specific spectra for both types of BG coatings, with three strong broad bands positioned at 764, 915 and 1020 $cm^{-1}$ respectively (fig. 1-a& b). The absorbance spectra were compared to the values given in literature [12, 13]. They were identified as follows:

- The maxima positioned 1020 $cm^{-1}$ and respectively 1040 $cm^{-1}$ are attributed to the *Si-O(s) asymmetric stretching* mode, located in the range 1000-1200 $cm^{-1}$;
- *Si-O(b) bending mode* is found at 764 $cm^{-1}$;
- The bands at 879 and 915 cm-1 could be associated to the *Si-O(s) stretching with one non-bridging oxygen (Si-O-NBO)* per $SiO_4$ tetrahedron ($Q^3$ groups);
- The bands at 839 $cm^{-1}$ and 850 $cm^{-1}$ are assigned to the *Si-O(s) stretching with two non-bridging oxygen* (Si-O-2NBO) per $SiO_4$ tetrahedron ($Q^2$ groups).

The presence of IR bands associated to Si-O-NBO and Si-O-2BO groups indicate that the vitreous silica network suffers a net decrease in its local symmetry by the addition of alkali ions or/and alkali earth ion (Na, Ca). This is in agreement with the EDS analysis that shown an increase of alkali content in the bioglass structure.

One can notice that the two BG films spectra differ by their *Si-O-NBO/Si-O(s)* intensity ratio. The BG-2 film shows an increased concentration of the Si-O bonds with non-bridging oxygen in comparison with the Si-O bonds with bridging oxygen as revealed by the corresponding peaks at 915 $cm^{-1}$ and 1020 $cm^{-1}$ in the FTIR spectra (fig. 1-a). A *Si-O-NBO/Si-O(s)* intensity ratio higher than 1 would presumably offer good bioactivity features of the BG structure in contact with body fluids [14].

Previous IR studies noticed also the presence of $Q^2$, $Q^1$, and $Q^0$ phosphate units in the 1400–400 $cm^{-1}$ IR spectra range [12, 15].




| a | b |
|---|---|

Fig. 1: a) FTIR spectra for as deposited BG1 and BG2 structure vs. target powder; b) FTIR spectra for BG2 abrupt structures and respectively BG2 graded structures

In fig. 1-b are presented in comparison the spectra of the BG2/Ti abrupt and respectively $BG2/BG_{1-x}Ti_x/Ti$ graded structures annealed at 700°C/2h in environmental air.

One can notice for all the annealed samples an absorption envelope with sharper shoulders than in case of as deposited samples IR spectra. Such a behavior is expected after the heat treatments, and corresponds to the inducing of a crystallization process in bioglass structure.

For both types of BG coatings a small shoulder at 1075 $cm^{-1}$ emerged as a consequence of modification in the crystalline/amorphous phase ratio. This band corresponds to the to $\nu_3$ asymmetric stretching of $(PO_4)^{3-}$ groups.

Important differences of FTIR overall intensity area can be observed between the BG graded structures and respectively the BG abrupt structures. The decrease of the intensity for the latter can be correlated to the pealing-off phenomena and possible compositional in-homogeneities. The shift to lower wave numbers of Si-O(s) absorption band suggests a strong mechanical stress in these films.

*3.4 SEM analysis of heat-treated BG-2 abrupt and respectively graded coatings*

Scanning electron micrographs were made on abrupt, respectively graded BG structures. Both types of as-deposited samples revealed a compact structure with a uniform and smooth morphology. The presence of light color sprinkled prominent aggregates was noticed for both types of films. These aggregates might be owned to the germination of some titanium oxides in the BG micro-pores that rapidly grow-up towards the more oxygenated layer surface. This hypothesis was confirmed by the EDS measurements that evidenced that the white areas are strongly enriched in titanium.

In case of abrupt structures, local peel-offs phenomena were evidenced (fig. 2-a, b), these areas being estimated at an average value of ~15% from the total film surface. Such morphologic defects could be owned the difference between the thermal expansion coefficient of the glass-ceramic layer and of the titanium substrate. It is widely accepted that both mechanical properties and chemical composition are important factors in the preliminary physiological bond of such implants. Low mechanical properties are the major problem that prevented the use of BG/Ti structures for load-bearing applications.

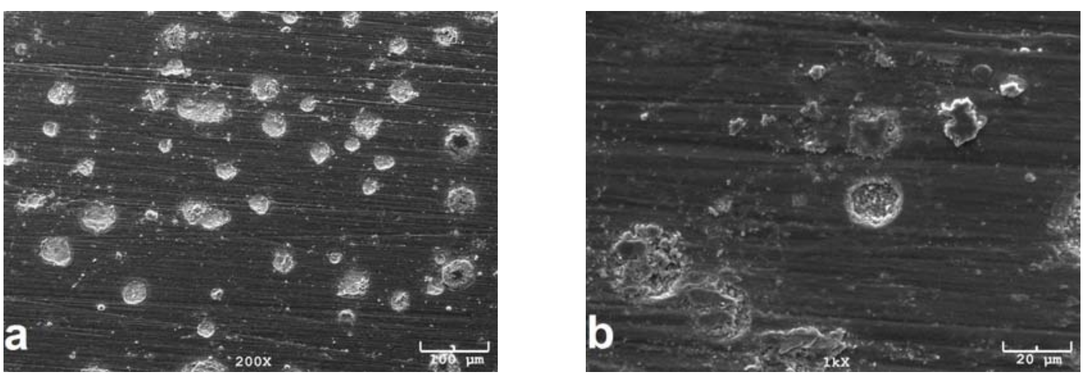



Fig. 2: SEM images of a BG-2 abrupt structure deposited on Ti substrate by magnetron sputtering and heat treated post-deposition at 700°C/2h: (a) panoramic view (b) detail

The SEM results are in agreement with FTIR spectra that shown a decrease of overall intensity in case of abrupt BG2 coatings.

One the other hand the annealed BG graded structures appeared more homogeneous, no exfoliations or cracks (fig. 3-a, b) could be observed. The titanium oxides seem to form on the BG coating surface without damaging its integrity.

This suggests that functionally graded buffer layer introduced attenuates the materials interface discontinuity, increasing the substrate/layer adhesion strength.

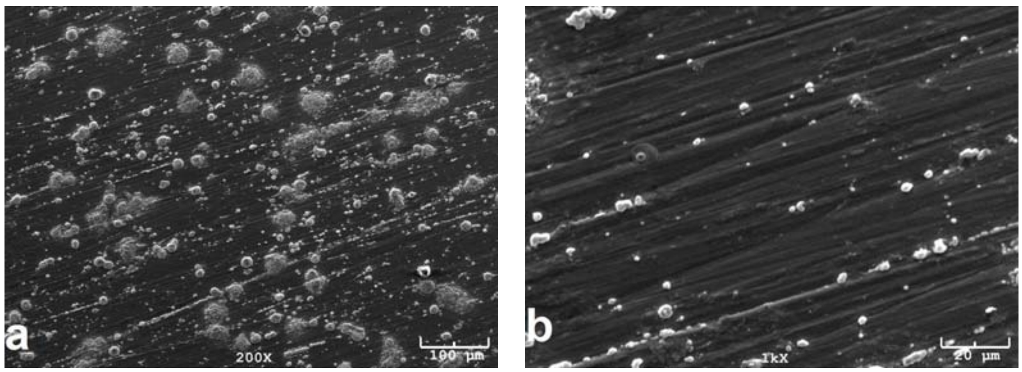



Fig. 3: SEM images of a BG-2 graded structure deposited on Ti substrate by co-sputtering and heat treated post-deposition at 700°C/2h: (a) panoramic view (b) detail

## 4. Conclusions

Bioglass films were successfully deposited by magnetron sputtering and co-sputtering techniques onto titanium substrates. The best results in terms of stoichiometry were obtained for the higher sputtering pressure (0.45 Pa). The FTIR results showed an increase of alkali content in the bioglass structure by the modification Si-O-NBO/Si-O(s) intensity ratio with increasing pressure. For the BG-2 films the Si-O-NBO/Si-O(s) intensity ratio was higher than 1, a prerequisite of bioactivity in contact with body fluids.

The effect of annealing was studied on the abrupt and respectively graded BG-2 structures. In case of abrupt films the thermal stress and the appearance of titanium oxides on the surface has strongly weakened the BG/Ti interface. In case of graded BG structures after annealing the films morphology appeared more homogenous without cracks or peel-offs.

These results have shown that the structures with functional compositional buffer layer showed certain promises and could be a viable solution in order to increase the substrate/bioglass coating adhesion. Pull-out adhesion measurements and bioactivity tests in simulated body fluid are intended in the near future.

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