The role of the reactive atmosphere in pulsed laser deposition of bioactive glass films

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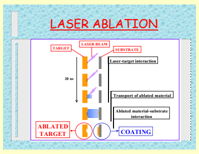
INTRODUCTION

AIM

To study the role of the **reactive atmosphere** (H_2O, NH_3, N_2O and Ar) and the **total pressure** on the PLD bioactive glass films properties.

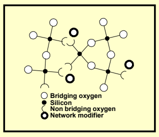
PULSED LASER DEPOSITION



- Absence of contamination.
- Growth of materials with high melting-point.
- Stoichiometry transfer of target composition.
- Fine control of the coating properties.

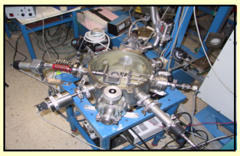
BIOACTIVE GLASSES

- Biomaterials based on silica glasses.
- The incorporation of ions (Na^+, K^+, Ca^{2+}…) act as network modifiers.
- Certain compositions of bioactive glasses present bone regenerative capacity.



- Open amorphous structure.
- Network modifiers: Na^+, K^+, Ca^{2+}.
- Disruption of the continuity of the glass network.
- Formation of non bridging oxygen groups (SiO-NBO).

EXPERIMENTAL



LASER ABLATION SYSTEM

- ArF excimer laser: 193 nm.
- Energy density: 4,17 J/cm^2.
- Repetition rate: 10 Hz.
- Rotation rate: 3 r.p.m.
- Base pressure: 7x10^{-5} mbar.
- Substrate temperature: 200ºC.

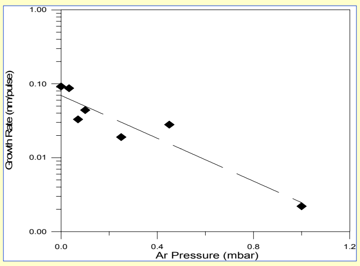
MATERIALS AND METHODS

- **Target**: Bioactive glass (42% SiO_2, 20% Na_2O, 20% CaO, 10% K_2O, 5% MgO, 3% P_2O_5)
- **Substrate**: Silicon.
- **Reactive atmospheres**: H_2O, NH_3, N_2O and Ar (UHP grade).
- **Characterization Techniques**:
  - Fourier Transform Infrared Spectroscopy (FTIR).
  - X- ray Induced Photoelectron Spectroscopy (XPS).
  - Profilometry.

RESULTS

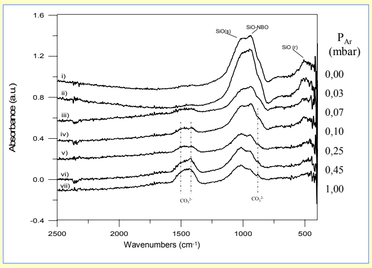
(A) INFLUENCE OF THE TOTAL PRESSURE

Growth rate of thin films



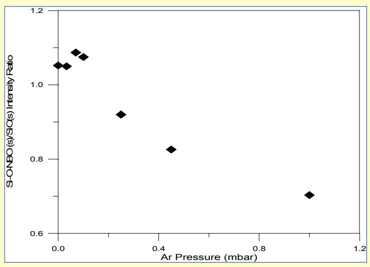
- Film growth decreases when the total pressure is increased.
- An exponential dependence was found.
- The background gas alters the expansion dynamics of the plume promoting the deceleration of the ablated species.

FTIR absorbance spectra



- The typical peaks of the bioactive glass can be observed.
- When the Ar total pressure increases:
  - The position of the absorbance band maximum of the SiO(s) vibration shifts towards larger wavenumbers.
  - The peak of the Si-O-NBO groups decreases and becomes broader.
- New bands associated to carbonate groups are identified.

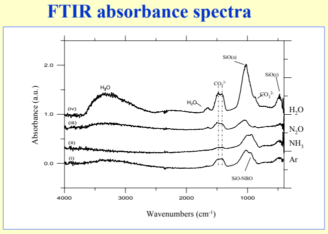
Si-O-NBO(s)/SiO(s) absorbance intensity ratio



- A minimum concentration of Si-O-NBO groups (NBO/SiO ≈ 1) is required in order to obtain an efficient bioactive process.
- Bioactive glass films deposited in vacuum or at very low Ar pressures present an optimum concentration of Si-O-NBO groups.

(B) INFLUENCE OF THE REACTIVE ATMOSPHERES

FTIR absorbance spectra



Ammonia atmosphere:

- The formation of the Si-O-NBO groups is promoted.
- The NH_3 dissociation by the UV photons leads to:

$$NH_3 + h\nu \rightarrow NH + H_2$$
$$NH_3 + h\nu \rightarrow NH_2 + H$$

- The presence of H radicals avoid the saturation of Si-O-NBO groups.

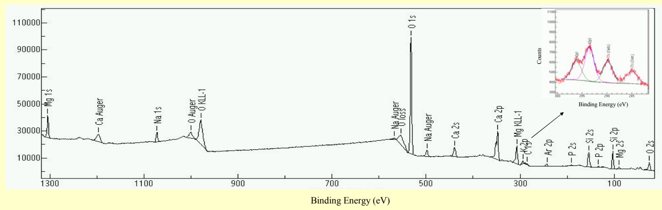
Oxidant atmospheres:

- The bands associated to Si-O-Si (s) vibration increase and the position of the maximum absorbance shifts towards larger wavenumbers.
- The Si-O-NBO groups are dramatically reduced.
- Two new bands identified as adsorbed water can be observed.
- These effects are related to the presence of oxygen radicals in the atmosphere due to the N_2O and H_2O dissociation by the ultraviolet photons:

$$H_2O + h\nu \rightarrow H + OH$$
$$H_2O + h\nu \rightarrow H_2 + O$$

(C) XPS STUDY OF CARBONATE GROUPS

XPS spectrum of a bioactive glass coating (0.45 mbar Ar pressure)



- All the components of the bioactive glass target have been identified.
- Two C_{1s} photoelectron peaks are observed:
  - The first at 285 eV is due to the absorption of hydrocarbon impurities and disappear quickly with the sputtering process.
  - The second is located around 289,8 eV which can be associated with carbonate groups: CO_3^{2-} (289,8 eV), $CaCO_3$ (289,6 eV) or Na_2CO_3 (289,4 eV).

CONCLUSIONS

- Reactive Pulsed Laser Deposition allows a fine control of the bioactive glass coating properties with medical interest.
- The total pressure plays an important role in the film growth and bonding configuration:
  - a) Film growth rate decreases exponentially with the pressure
  - b) Coatings grown at low pressures show an optimum concentration of Si-O-NBO groups.
- When the ablation experiments are conducted in an oxidant environment, the reduction of the Si-O-NBO groups and incorporation of adsorbed water is promoted.
- The presence of an ammonia atmosphere favours the formation of Si-O-NBO groups an it allows the tailoring of coatings with an appropriate biological response.