

Compositional optimization of bio-functional doped-Carbon thin coatings grown by advanced pulsed laser techniques for biomedical applications

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The development of innovative solutions for surface modification of medical implants is a hot-topic nowadays, and represents the main objective of this application. A promising alternative to achieve this goal is the synthesis via advanced pulsed laser techniques of biocompatible thin films such as carbon coatings. The incorporation of two functional elements (Ag and Si) into very biocompatible material as the carbon coating is, will allow obtaining very good, novel materials from both physical and medical point of view. Synergetic interaction between carbon coating and doping elements will provide a rise in biocompatibility, optimal release of microbicidal ions providing increased resistance to microbial colonization and protection against consequent medical devices biofilm associated infections as well as acceleration of the osseointegration process what is evidence of multi-functionality. However, the major challenge to be addressed in this project is to find the optimum dopant concentration values as well as their 3D spatial distribution.

Diamond Like Carbon (DLC) films have a wide range of applications due to their good mechanical, tribological, chemical properties and chemical inertness. These films are also of interest in the biomedical applications due to their high biocompatibility and hemocompatibility. Integrity and durability of the coatings lead to creation of diffusion barriers against harmful metal ions that are components of the implant material, which significantly limits the occurrence of allergic complications. However, high internal stresses in the hard DLC films coupled with low adhesion to relatively soft materials such as titanium alloys become an extremely important problem in the implantology. To reduce the residual stress and to enhance the adhesion and tribological properties of the DLC films, incorporation of metals which form carbides such as Ti, Mo, Cr, W, Si as well as elements that do not form carbides (like Cu and Ag) are extensively studied.

In addition to the above mentioned properties, Si-doped DLC coatings provide also good thermal stability, reduced hydrogen loss, graphitization, resistance to oxidation, moisture and corrosion as well as low wettability. Recently, it was reported that Si incorporated DLC (Si-DLC) films exhibit very low friction coefficients of about 0.05 in various test environments. Moreover, many scientists proofed that mechanical properties of Si-DLC films such as hardness, elastic modulus and residual stress were increased by Si addition. Such dependence is kept when the amount of Si in the coating does not surpass 5%, above this content the “saturated behaviour” phenomena is observed. It is demonstrated that the coatings with Si could render the surface antithrombogenic by inhibiting the fibrinogen activation and have bacteriostatic properties. Among the different deposition techniques, the most widely used has been plasma enhanced chemical vapor deposition (PECVD).

Ag incorporation in the DLC films reduces surface free energy and residual internal stress without sacrificing the hardness, increases in hydrophobic properties and enhanced the electron field emission property with lowering the work function. So, the Ag-DLC coatings exhibit strong hemocompatibility and wide range microbicidal effect. It has also been reported that the tribological properties of DLC films can be improved by doping with Ag. Ag-DLC has demonstrated low coefficient of friction and high wear resistance. In literature it is mainly described that silver in the carbon coating is obtained using Magnetron Plasma Source Ion Implantation method or magnetron sputtering.

Pulsed laser technologies have proved extremely versatile to synthesize a wide range of materials (simple, complex, and/or doped). It is rather easy to implement these methods which stand for a compelling alternative for depositing bioactive, biocompatible, antimicrobial, highly adherent, uniform thin films from a broad variety of materials used in implantology and surgery as a whole. Laser technologies are efficient, free of pollution due to the use of light sources for deposition and readily adaptable to different geometries and complex structures. Two complementary laser-based techniques will be implemented in these studies: Combinatorial Pulsed Laser Deposition (C-PLD) and Combinatorial Matrix-Assisted Pulsed Laser Evaporation (C-MAPLE).

Combinatorial Pulsed Laser Deposition (C-PLD) technique will be used for controlled doping and synthesis of advanced libraries of Ag:Si-DLC, in a single-step process to facilitate the search for optimum dopant concentration values. The main difference with respect to conventional PLD, is that in the case of C-PLD the laser beam is divided into two beams (Fig. 1) by an optical beam-splitter. The two beams are separately directed by mirrors and focused by lenses inside the deposition chamber onto the surfaces of two or more targets. Accordingly, on the facing substrates we will obtain a perfectly controllable gradient of composition along the longitudinal direction from almost 100% of a material A (e.g. DLC) to almost 100% of a material B (e.g. Ag and/or Si dopant) over well-defined areas, by changing the separation distance (D) between targets, or the specific irradiation sites. Our expertise in this direction was mainly applied in case of IZO compositional libraries for tuning the structural, optical and electrical properties [1,2], in case of materials with complex stoichiometry like calcium phosphates doped with Ag for biomedical applications [3], but also for the synthesis of biopolymer compositional gradient thin films by C-MAPLE [4,5].

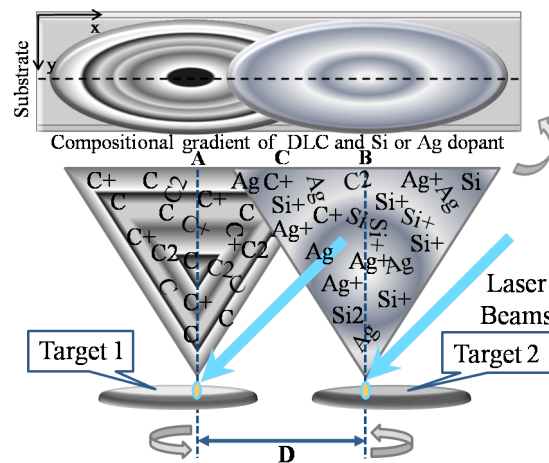


Figure 1 Typical set up for Combinatorial Pulsed Laser Deposition

C-MAPLE is close to C-PLD, the main difference consisting in target preparation, since was mainly applied to organic thin films synthesis. Accordingly, usually the irradiation doses or fluence used during laser ablation is one order of magnitude lower. C-MAPLE will be considered as an alternative solution to C-PLD due to its capability to be used in case of inorganic materials as well, as it was proved to allow for obtaining high quality thin films.

Two batches of combinatorial (Ag+DLC and Si+DLC) samples will be deposited from three targets (Ag, Si and pyrolytic graphite) using two laser systems (KrF* or Nd:YAG). A compositional library will be generated for each combinatorial pair. The experimental conditions (laser fluence, number of pulses, repetition rate, target-substrate separation distance, ambient pressure inside reaction chamber, substrates temperature) will be optimized in order to obtain the best quality coatings.

However, the precise investigation of the dopants concentration along the longitudinal direction of the samples as well as their 3D spatial distribution is mandatory. Since complementary characterization techniques suffers due to limited accuracy (EDAX), or very limited depth resolution (XPS), the chemical stoichiometry of the grown films is very important and must be achieved using a reliable technique such as Rutherford Backscattering Spectrometry (RBS) or non-Rutherford Backscattering Spectrometry (NRBS).

RBS with light ions, typically 1–2 MeV ^1H or ^4He ions, is the most used technique for depth profiling of elements concentrations. Moreover, under channeling conditions, this technique may be used in order to obtain information about the sample structure and lattice as well as locations of impurities. Channeling is a powerful procedure widely used for the characterization of ordered samples.

^4He particles up to several MeV have been considered as most convenient projectile for materials characterization purposes by elastic backscattering. This regularly gives sufficient mass and depth resolution. However, the complex film structures with several compound materials, require large/higher mass and depth resolution.

The RBS technique presents some limitations. Among these, we mention poor mass resolution for heavy elements and sensitivity for light elements. In addition, the mass determination is not definitely possible, except for the surface. The analysis of light elements in a heavier matrix is frequently impossible, because of the energy overlap of the beam ions scattered by light surface atoms and by heavier bulk atoms deeper in the sample. Besides, small amounts of light elements are difficult to analyze, because the Rutherford cross-section has a Z^2 dependence.

It was demonstrated that the mass and depth resolution, as well as the sensitivity may be improved via heavier and more energetic ions. In particular, mass separation for medium and heavy elements is improved significantly when using heavy RBS ions. The energy separation in function of the projectile mass M_1 , the projectile energy E_0 and the target mass M_2 is:

$$\Delta E \cong \frac{2M_1E_0}{M_2^2}(1 - \cos\theta)$$

where θ is the backscattering angle. This is valid for $M_1/M_2 \ll 1$. The expression requires the use of higher mass projectiles and bombarding energies. There are, however, several drawbacks. These are related to worsening of the resolution of the silicon detector due to

$1/E_0^2$ dependency of the cross section when the counting rate reduces. Consequently, when higher energies are needed it is required a longer analyzing time. In order to avoid these shortcomings, we can use a time of flight spectrometer.

A severe disadvantage of conventional RBS is the low sensitivity in case of light elements. The Rutherford scattering cross-section is proportional to the square of the nuclear charge of the target nucleus. Therefore, due to backscattering from heavy elements in the sample, the scattering peaks from light elements such as C, N and O are superimposed on a relatively high background. Recently, high energy ^1H and ^4H backscattering has been used in order to overcome this drawback and to correctly quantify the stoichiometry or to profile the light elements in the heavy bulk samples. In these experiments, ^1H and ^4He ions of 3–9 MeV (or even more) are used as high energy backscattering incident projectiles. The elastic Rutherford scattering cross-section for light elements becomes a nuclear interaction, called non-Rutherford backscattering or nuclear resonance elastic scattering. The non-Rutherford backscattering can be therefore used to improve/boost the sensitivity for light elements. For example, when using ^4He with energies of 3.045, 4.265 and 3.72 MeV, the elastic backscattering cross sections for O, C and N are of 25, 150 and 6 times larger than their corresponding Rutherford cross-sections, respectively.

We plan to use RBS and NRBS techniques to characterize the thin layers of the Ag+DLC and Si+DLC. Both RBS and NRBS with 4.5 MeV ^4He will be used. The measurements will be carried out in a dedicated target chamber. The experiments will be performed at 3 MV Tandatron accelerator using a standard backscattering setup. First of all, the energy calibration of the ^4He beam used for measurements will be done. The method currently used for the calibration of the analyzing magnet fields of the tandem accelerator consists in comparing the energies of alpha particles from a radioactive source with the energies of ^4He projectiles back-scattered into a silicon detector by thin carbon and gold layers. The ions scattered at 165° will be detected by a Si detector having 17 keV resolution. We need 3 days (9 shifts).

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