Laser produced coatings and surface modifications for medical implants

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Abstract. Lasers can be an effective tool for tailoring the surface of medical implants. Laser irradiation can modify the surface wettability, bioactivity and its capacity to absorb proteins. By using appropriate energies and wavelengths, also the topographical features at macro, micro and nano level can be shaped in order to adapt to cells, extracellular matrices and orientation of ligand molecules. Pulsed laser deposition can produce nanometer thick, dense and well adhering CaP coatings with extremely fine control of chemistry and crystallinity. No further thermal annealing is needed. In-vitro and in-vivo experiments with different cells and animals models have demonstrated similar or better osseointegration of laser deposited coatings compared to the commercial available plasma sprayed ones. Ultraviolet lasers can successfully chemically functionalize the surface of implants, and femtosecond laser can drill polymer plates or meshes for tissue engineering applications.

1. Introduction. The surface of medical bone implants.
A 2003 estimation of the orthopaedic worldwide market amounted 14.2 B€, while the global dental market was estimated to be 1.200 M€ in 2004. Growth rates for both were predicted to be 13-18% annually. In orthopaedics this means worldwide some 2 million hips and 1 million knee implants, with around 300,000 revisions per year. A recent 2010 study [1] confirmed the optimistic predictions of the last decade by estimating presently the US implantable medical device market in $33 billion and in spite of the present economic crisis still they forecast an 8.3% annually growth through 2014.

When implanted, any medical bone substituting device interacts with the body in the initial stages primarily through its surface. Therefore it is of utmost importance to control, design and engineer the surface of implants in order to obtain a fast osseointegration with a long lasting fixation [2]. Thus, all steps in the series of events taking place after implantation are to be tackled for optimization of the correct body response: the protein adsorption into the surface, cell arrival and adhesion to the surface, cell differentiation, proliferation and communication, the secretion of extra cellular matrix (ECM) and later vascularization of the new tissue.

Among the characteristics of an implant surface that will determine its performance in the body, the surface energy determines the wettability of the surface, of great importance since implants are first of all in contact with the water based body fluids. Moreover, depending on the chemical composition of the surface, some glasses and ceramics show bioactivity [3], a time dependent kinetic modification of the surface upon implantation, stimulating surface reactions and leading to bone bonding. Protein adsorption takes place in a time scale from less than a second to minutes for the formation of a monolayer of adsorbed proteins well before cells arrive at the surface. These proteins either promote or prevent cell adhesion.

Moreover, the size and geometry of features must be congruent with the cell morphology, its size, its anchorage focal points and the later formation of extra cellular matrix that will fill the spaces and serve as attachment structures for proteins and cells. In addition, roughness determines the surface area offered for interaction with the environment. Recently nano-roughness has been found to affect the orientation of ligand binding molecules, and therefore modulating their efficiency.
2. Laser processing of surfaces

Lasers can be an effective tool in tailoring the previous mentioned properties of an implant surface for achieving best in-vivo performance, such as laser oxidation of the surface of titanium and its alloys, macro- and micro-structuration of metallic and polymeric implant surfaces [4], laser drilling of polymer plates or meshes for tissue engineering applications using femto-second lasers [5], pulsed laser deposition (PLD) of bioactive very thin coatings [6] or grafting of amine groups on the surface of polymers [7].

2.1 Bioactive coatings

Different research groups have optimized the deposition conditions for production of thin calcium phosphate coatings [6]. Great effort has also been dedicated to understand the processes occurring as the material is transported from target to substrate, in search of scientific bases for the optimization of the coatings beyond empirical work. It has been demonstrated that pulsed laser deposition can produce very thin, dense, well adhering coatings, with extraordinary controlled chemistry and crystallinity. Compared to other deposition techniques, PLD offers several advantages:

- Congruent deposition may be obtained. Different calcium phosphate phases with and without diverse substitutions, and morphologies can be deposited, so that the degree of resorption may be adapted to a specific medical application. Coatings with graded composition, or graded crystallinity can readily be produced.
- No post-deposition thermal annealing is needed, thus the coating-metal interface remains strong adherent.
- Film thickness can be very well controlled, simply by turning the laser on and off.
- The possibility of coating is not limited to metal substrates, but polymer surfaces can also be coated, via either a pre-treatment or modifications of the PLD technique.

![Push-in Test](image)

**Figure 1.** Mean shear strength of titanium cylinders with different surface treatments after implantation in dog jaw (3 months).
In-vitro and in-vivo testing have verified similar or better osseointegration of the pulsed laser deposited hydroxylapatite (HA) films than the commercial available plasma sprayed coatings, but with improved adhesion properties, without risk of delamination or detachment of the coating, as can be the case with the commercial plasma sprayed technique. Fig. 1 depicts the mean shear strength obtained in a push-in test for cylindrical samples that were implanted for three months in dog jaw. Five types of surfaces were tested: smooth as-machined titanium (Ti-s), grit-blasted titanium (Ti-g), plasma sprayed coated HA (PS), pulsed laser deposited HA on grit-blasted titanium (PLD-g) and PLD coatings on smooth titanium (PLD-s).

Surface roughness lead to higher shear strength, due to mechanical interlocking. The PS coating did not improve bonding compared to grit blasted Titanium, probably due to internal fractures within the thick coating when subjected to load. PLD improves bone-bonding (both on grit-blasted and smooth surfaces) in agreement with histomorphometrical findings, whereby more bone apposition was found on the PLD coated samples.

Therefore, the technique is mature for an industrial scale-up on the one hand and the start of clinical tests with real implants on the other hand. Commercial dental implants and orthopaedical spine screws have been coated with HA using ArF laser- demonstrating the uniformity of the coating thickness around the corners and sidewalls of implant devices.

2.2 Chemical functionalization
193-nm excimer laser have been applied to chemically grafting of ammonia on poly(ethylene terephthalate (PET) films. Surface chemical patterning was performed by irradiating PET film in a vacuum chamber filled with ammonia at different fluxes. While the hydrophilicity of the surface increased after patterning and a minimum water contact angle was obtained at the gas flux of 20 ml/min, roughness remained unchanged. TOF-SIMS ion mapping was used to identify the amine containing fragments corroborating that amino grafting mainly happened inside the laser irradiation area of the PET surface. A hypothesized radical reaction mechanism proposes that the collision between the photolytic decomposed radicals from ammonia and those on the PET surface caused by the incident laser provokes the grafting of amino groups.

3. Conclusions
Lasers can be an effective tool for tailoring the surface of medical implants for its variety in wavelengths, pulse lengths and pulse energies. Depending on these parameters, lasers can remove or topographically shape the surface without modifying its chemistry, or chemically vary the surface composition, allowing its chemical functionalization and patterning, locally or in great areas, without compromising its topography.

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