PULSED LASERS APPLICATION IN BIOMEDICAL FIELD

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INTRODUCTION

In the mid-19th century the Czech physiologist Jan Evangelist Purkinje introduced use of the Greek word plasma (meaning ”formed or molded”) to denote the clear fluid which remains after removal of all the corpuscular material in blood. Half a century later, the America scientist Irving Langmuir proposed in the 1922 that the electrons, ions and neutrals in an ionized gas could similarly be considered as corpuscular material entrained in some kind of fluid medium and called this entraining medium “plasma” [01]. However unlike blood that is really a fluid medium carrying corpuscular material, the plasma is not fluid medium but a gas where the most part of the atoms or molecules are ionized. Plasmas are complex and exist in a wide variety of situations differing by many orders of magnitude. As plasmas do not normally exist is ordinary human experience, people do not have the sort of intuition for plasma behavior that they have for solids, liquids or gases. An idea of plasma could be when gas is raised to a sufficiently high temperature, and the atoms and molecules of the gas may become ionized. The electrons escape from atom by means of collisional process between particles, being the thermal agitation of the particles increased. When this happens, the dynamical behaviour of the gas may be dominated by the electromagnetic forces acting on free ions and electrons, and its properties become sufficiently different from those of a normal unionized gas to merit the introduction of name plasma [02]. The fundamental parameters of the plasma are:

1. the particles density $n$ (measured in particles per cubic metre);
2. the temperature $T$ of each species (usually measured in eV, where 1 eV=11.605 K);
3. the steady state magnetic field $B$ (measured in Tesla).
Other parameters as Debye length, plasma frequency, cyclotron frequency, thermal velocity can be derived from these three fundamental parameters [01]. For partially-ionized plasma, the fractional ionization and cross-section of neutrals are also important.

Examples of terrestrial plasmas are arcs, neon signs, fluorescent lamps, welding arcs and lightning that have electron temperature of a few eV and ion temperature that are colder. Typically, these plasmas are weakly ionized and dominated by collisional and radiative processes with densities that range from $10^{14}$ to $10^{22}$ m$^{-3}$ (for comparison, the density of air at STP is $2.7 \times 10^{25}$ m$^{-3}$) [01].

At the present time, one of the most important branches of plasma research is in the area of controlled thermonuclear fusion [03]. Essentially, the goal of this program is to make a miniature star on earth, generating energy by means of the same reaction that takes place in the sun. The fundamental process is that of the nuclear fusion of heavy isotopes of hydrogen into helium, with the subsequent release of energy. In order to achieve the fusion process, the reactants must be heated (to some millions of degrees) and then kept together in sufficient concentration for a period of time to allow the reaction to become exothermic [04]. Fusion researchers have succeeded at to realize fully ionized hydrogen or deuterium plasmas and they have reached temperatures in the range from 10’s of eV to tens of thousands of eV.

In typical magnetic confinement devices (e.g.: tokamaks, stellarators), the plasma particles are affected by an externally magnetic field (1-10 Tesla) with carefully chosen geometry imposed on the plasma [03]. Controlled fusion can be achieved by having a large number of hot plasma particles together for a short period of time or a smaller number of particles together for a longer period of time. That is, the product of plasma
density multiplied confinement time must be roughly a constant (Lawson
criterion).
In these conditions of magnetic confinement, the reached densities are
situated in the range $10^{19}$-$10^{21}$ m$^{-3}$ [04].

The other side, we have the Inertial Confinement Fusion (ICF) that,
historically, has been the main application of laser-produced plasma and
the main motivation for research in the field of the commercial generation
of electricity by thermonuclear fusion [03]. Also here, heavy isotopes of
hydrogen are heated to temperature of around 10 keV where the nuclei
have sufficient energy to penetrate the Coulomb potential barrier and to
ignite the nuclear reactions.
Plasmas used in inertial fusion are much denser, the goal is to attain for a
brief instant densities of one or two orders of magnitude larger than solid
density ($\sim 10^{27}$ m$^{-3}$) [01].

Covers, instead, an enormous range and are lowest the densities of the
space plasma. These plasmas vary from $10^6$ m$^{-3}$ in interstellar space, to $10^{20}$
m$^{-3}$ in the solar atmosphere [01]. While, the temperature range from 1 to
100 eV and are usually fully ionized.
The equilibrium state is another fundamental characteristic of the
plasma. In particular, is the absence of equilibrium that makes the plasma
very interesting. Concerning this, we can describe briefly three kinds of
equilibrium conditions commonly encountered in plasmas [05].
The first type of equilibrium is the simplest in a sense and is the
“ultimate” equilibrium when all plasma constituents (various ion species,
electrons, neutrals species, and radiation) are in equilibrium with one
another. The energy distributions of ions and electrons are Maxwellian and
the emitted radiation has a black body profile. Under these conditions, the
only relevant parameter is the common value of the temperature fully
characterizing the black body radiation profile as well as the energy
distributions of electrons and ions of all types. Equilibrium is established by collisions and in this case any outside radiation becomes trapped in the plasma.

A second type of equilibrium is known as local thermal equilibrium (LTE) [06]. Here we are looking at the abundances of ions in various electronic states. In addition to the temperature, the actual atomic energy level structure becomes important, since these populations are related to each other by Boltzmann factors (between levels within the same ionization stage) and the Saha equation (across ionization stages). LTE occurs in dense plasmas where collisional atomic processes (electron-impact excitation, etc.) dominate over non-collisional processes (spontaneous radiative decay and auto-ionization) [06].

In diluted plasmas, we encounter a third kind of equilibrium where the population of the ionized states is independent of electronic density. This is corona equilibrium (example in astrophysics are the interstellar nebulae and sun’s corona from which the name) which is quite rarefied plasma. Under such low-density conditions, collisional excitation cannot keep up with radiative decay leaving excited states essentially unpopulated. The overall ionization balance is then determined by the competition between collisional ionization and recombination processes linking the ground states of neighbouring ionization stages [05].

Plasma may be close to either one of these three limits cases but in many situations it is somewhere between them. However when many effects are of comparable importance, the problem cannot be simplified by discarding the effects weaker without to commit significant inaccuracies. Different are the complications present in the plasma, because of the populations and rates of atomic processes that are mutually dependent [02].

Among many applications of laser-produced plasmas, some applications require small lasers only, other is characterized by employed
of very high power lasers (e.g.: Inertial Confinement Fusion) [03]. This work will focus on plasmas produced by laser of low power and in particular on applications of pulsed laser in biomedical field.

In medical field, the interaction between the electromagnetic radiation and the biological tissue it is a phenomenon very complex since involves different physical aspects and different biological reactions. In fact, the tissue ablation is a non-liner interactions where the physical properties of tissue do not remain constant during the laser radiation. A wide range of tissue reactions can be achieved by varying the laser pulse duration, energy per pulse, wavelength and spot size. In each case, the amount of energy absorber in a specific volume is critical [07]. In general, the transfer of the light energy into a tissue depends on three factors:

1. The wavelength of the laser light;
2. The power density of the laser;
3. The chemical and physical properties of the target.

The strong absorption tends to minimize the thermal damage to the underlying areas because the diffusion of heat from the laser photons is minimized [07]. Also the lasers with shorter pulses minimize the lateral spread of heat or thermal damage.

The selection of the laser from using, is seriously conditioned from wavelength of the laser. The wavelengths of infrared photons correspond, in energy, to vibrational and rotational sublevels of excitation of the molecules of all biological tissues. This mode of energy transfer is known as “heat”, and is rapidly redistributed among the molecules and raises the temperature of target tissue until the boiling point of the water [07]. Short-pulsed lasers with wavelength in the near-infrared such as Er:YAG, Ho:YAG and Er,Cr:YSGG can be well absorbed by the water component [08].
Fundamentally different are the **photochemical effects** due to absorption processes. Absorption UV leads to ionization processes and excitation of the electrons that hold the atoms of the structural molecules together. This phenomenon conveys the energy of the photon directly to the bonding electrons and facilitates the break up of these bonds [07].

If the photons are of ultraviolet wavelength, the energy ($h\nu > 3 \text{ eV}$) is exclusively absorbed by the proteins that are subjected to bond-breaking and following ablation. The water content is expelled mostly in a liquid state together to the pieces of protein and its gaseous products. If, instead, the photons are of infrared wavelengths ($h\nu < 1 \text{ eV}$), it is the water that absorbs most photon energy to produce steam. The resulting explosion tears the protein filaments apart. Therefore, the process of photon energy transfer into target can be separated into three individual steps:

1. absorption of the photon;
2. bond breaking;
3. ablation of the target tissue.

In this thesis, different applications of pulsed lasers are discussed in the ambit of biomedical field:

1. Laser-biological tissues interactions (H$_2$O, dental tissue, soft tissues), for medical applications;
2. Laser-material interaction (UHMWPE, PE, PMMA, PS, PTFE), for material structure modifications;
3. Laser deposition, of thin biocompatible films (Ti, HA, C, Al$_2$O$_3$);
4. Laser Ion Source, to prepare ion beams for hadrontherapy (C$^+$,H$^+$);
5. Laser Ion Implanter, to produce multi-energetic ion beams with 5 keV÷500 keV energy and high current density ($\sim 1 \text{ mA/cm}^2$) to implant different surfaces.

The ablation of the tissue consists of an explosion in miniature as a result of extremely fast pressure increase, photo-decomposition, and photo-
thermal effects. The ablative photo-decomposition, typical of the UV photons, is not a thermal reaction. In contrast, the vaporization is a thermal process that occurs with non-UV laser reactions. In addition to the obvious thermal effects and vaporization, there are many non-thermal effects such as recoil, pressure wave formation, ionization, free radical formation, photochemical induced oxidation, multi-photon absorption process and mechanically induced shock waves [09, 010, 011]. Of particular interest, it is the induced damage potential from shock wave to the artery wall. Shorter is the laser pulse, higher is the power density, and more violent is the force of ablation [07]. Using laser intensities of the order of $10^{10}$ W/cm$^2$, the pressure of the shock wave is about 100 MPa.

The most medical application for laser technology in medicine has been in ophthalmology. The lasers mainly employed are the argon (488.0 ÷ 514.5 nm), krypton (647.1 nm), argon pumped dye (577 nm), Nd:YAG (1064 nm), and most recently diode lasers. This lasers have achieved remarkable clinical successes in the treatment of retinal diseases, glaucoma, and lens capsule opacification following cataract surgery.

The use of laser as a selective heat source to coagulation retina tissue is one of the most important and widely adopted ophthalmic laser applications. It is a typical mechanism of photothermal laser-tissue interaction and occurs when laser energy is absorbed by the target tissue and is converted into heat. Another applications of the photothermal mechanism is the laser corneal surgery and laser tissue welding [032].

Nd:YAG laser operating at 1064 nm with short pulsed ($\approx 30$ ps for mode-locked and $\approx 10$ ns for Q-switched) is used to create optical breakdown and photodisruption of ocular tissue. The extremely high irradiances ($10^8$÷$10^{11}$ W/cm$^2$) brings to the development and to plasma creation that reaches peak temperature $\geq10^4$ °C [07].
Using a far-UV (193 nm) argon fluoride excimer laser is possible to remove the corneal tissue discretely and precisely without thermal damage of the adjacent tissue (corneal sculpting). This photoablation occurs because the cornea has an extremely high absorption coefficient at 193 nm, and the photon at 193 nm are highly energetic (6.43 eV). This energy is greater of energy than the carbon-carbon bonds interlinking the protein molecules of the cornea. Consequently, the intermolecular bonds are broken and the discrete volume of corneal tissue is removed with each pulse of the laser [033, 034].

A particular investigation discussed here, regard an application of pulsed laser in medical dentistry. Pulsed laser were introduced to dental research in the early 1960s and are now used in several specific areas of application, such as surgical treatment of oral malignancies and periodontal diseases, dental caries detection and control, preparation and sterilization of root dental canals [012]. In spite of these advances, laser are still limited in their ability to remove sound tooth structure since elevating the temperature in the tooth can generate adverse effects at the surface and in tooth pulp.

Er,Cr:YSGG pulsed laser operates in the infra-red spectrum at 2780 nm, shows a strong peak in the absorption spectrum of hydroxyapatite and water which leads to a high efficient ablation [08]. The hydroxyapatite (HA) has the Ca_{10}(PO_4)_6(OH)_2 chemical composition and is contained in the concentration of 97% in the dental enamel. The water content of enamel is about 2.5% and that of dentine 13%. These materials weakly absorb the radiation in the visible and near-IR spectral region where the laser irradiation causes thermally induced changes on the enamel and dentine surfaces [014]. Erbium laser, therefore, offers the ability to remove enamel, dentine and carious with minimal amounts of thermal disruption to the residual tooth.
The laser energy is delivered through a fiber optic system to a sapphire tip and is bathed in an adjustable air/water spray. Thus, the laser energy is strongly absorbed by the water micro droplets, which are partially responsible for the hard tissue cutting effects, as reported in literature and designated as HydroKinetic System (HKS) technique [015].

Another field of investigation of laser application has been the Pulsed Laser Deposition (PLD) technique. This technique permits to deposit biomaterials, metals, ceramics and polymer coatings in vacuum, preserving their original properties.

The innovative use of biomaterials to repair and reconstruct diseased or damage parts of the body has improved the quality and the length of the life for thousands of people. A biomaterial is a conceived material as interface with the biologic systems to evaluate, to give support or to replace an any tissue, organ or function of the body. Where the biocompatibility of a material consists into characteristic of establishing favourable interactions with the living systems which it comes in contact.

The most interesting substrate, in dental and orthopedic field, that may be coated with HA are Ti and its alloys, such as Ti₆Al₄ and TiAl₆V₄, and hydrogenated polymers, such as polyethylene (PE) and polymethylmethacrylate (PMMA). These implants coated with HA offer high mechanical integrity of a metallic device and high biocompatibility with the natural mineral composition of the bone [016, 018]. Carbon, titanium and polyethylene coatings improve the biocompatibility of the surface and modify significantly the chemical and physical properties of the covered surface. Carbon, for example, is hemocompatible and can be used for surfaces which are in contact with the blood, such as artificial blood vessels. Titanium oxide is inert and it can be employed for chemical passivation different surfaces, such as those in stainless steels. Polyethylene
is a hard polymer which can be used so as a shock-absorber of stresses or so as a repellent water surface [016].

In this investigation, the application of Pulsed Laser Deposition (PLD) technique is discussed using a Nd:YAG pulsed laser operating at different wavelengths. Laser light interaction with the target surface causes a very fast energy deposition in a thin surface layer with a consequent emission of vapor containing neutral, cluster and ion species. The energy of the particles ejected from the laser-generated plasma reach kinetic energy of the order of keV and their deposition produces ion implantation with a consequent high adhesion of the film to the substrate surface [017]. Increasing the laser fluence increases the ablation yield, the velocity of the film growth, on the substrate, and the adhesion of the film to the substrate surface.

Also the superficial modification induced by laser irradiation is employed with the aim to improve some chemical and physical properties of the polymer and to obtain a sort of anisotropic polymeric sheet useful for different applications [019]. Energetic pulsed lasers are capable to induce modification and micromachining in different polymeric materials with submicron precision without incurring thermal damage to the surrounding un-irradiated regions. With the short impulses of high intensity UV, visible and IR light laser, ablative photo-chemical and photo-thermal effects can be induced in the superficial layer of irradiated material producing scissions of chemical bonds, cross-linking and outgassing of volatile species [020-022]. A special attention is devoted to the processes that improve the polymer properties such as hardness, chemical and mechanical resistance and anisotropy. The laser ablation of these hydrogenated polymers is a function of the deposited energy while the ablation yield depends on the material absorption coefficient at the used incident laser wavelength [019].
The mechanisms responsible of the ablative photodecomposition of the irradiated polymer are the photochemical and photo-thermal involved effects. Depending on the properties of the irradiated material and the irradiation conditions, such as wavelength and pulse duration, one of them may become dominant. Generally, photochemical ablation occurs when incident photons have enough energy to bring the molecule in the excited electronically state, directly breaking main chain bonds. Energy absorbed in this bond-breaking process would restrict the temperature rise and the extent of thermal damage to the substrate. Instead, generally, the thermal ablation occurs when the incident single photon energy is not sufficient to break a single chemical bond. In this case, polymer chains bond breaking occurs for collective photon-molecule interactions [023]. Thermal processes can produce effective polymer ablation in which the photons couple to vibrational modes [019].

Laser effect in the nanocomposite depends on the carbon nanotube amount present in the material and on the irradiation time. Laser effect involved, anyway, only the external layers of nanocomposite, leaving the bulk unchanged. Nano-tube presence modifies the pristine polymeric properties increasing its hydrophilic character, decreasing its electrical resistance and, generally, increasing the material laser adsorption coefficient [019]. Therefore, the UHMWPE polymer can be treated efficiently by pulsed laser irradiation in vacuum, in order to modify the superficial properties of the polymer without change the bulk ones. Increasing the laser energy and/or the irradiation time it is possible to modify significantly the properties of pure UHMWPE and nano-tube doped polyethylene up to a depth of order of the hundred of micron [019].

Finally, a particular investigation has looked at the Ion Implantation and in particular new type of implanter, named Laser Ion Implanter (LII). In this study a Laser Ion Sources (LIS) is employed to produce non-
equilibrium titanium plasma, where the new ion source is obtained with a pulsed Nd:YAG laser operating in the power density region of $10^{10}$ W/cm$^2$.

Such ions, having different charge state, large range of kinetic energy (from eV to keV), Boltzmann-shifted energy distributions, high total current density, can be accelerated and focused in order to obtain multi-energetic ion beams with energies of the order of hundred keV, useful for ion implantation processes [024, 025]. The high-energy ions impinge on the substrate with kinetic energies 4-5 orders of magnitude greater than the binding energy of the solid substrate and form an alloy with the impact surface.

Generally, the implanted substrates include metals, ceramics, and polymers. The most commonly implanted metals include steels, titanium alloys, and some refractory metals, while implanted polymers include polyethylene at ultra high molecular weight (UHMWPE) for his wide use in different fields.

Some simulations (with MATLAB computer program) have been used to reproduce the experimental ion energy distribution and calculate the initial velocity of ions and the angle of going out respect to the normal direction of the surface target. Other simulations (with TOSCA-OPERA 3D) have calculated the percentage of ions hitting the substrate with respect to the total emission at the target. Finally, with SRIM (Stopping and Range of Ions in Matter) [026] has been possible to calculate the stopping and range of ions in substrate.

With this process, properties such as hardness, wear resistance, corrosion resistance, and fatigue may be altered according to the selected implantation element.

An application more experimental has regarded a superficial modification by multi-ion implantation in UHMWPE [030].
New devices made of polyethylene at ultra high molecular weight (UHMWPE), are employed in different fields (mechanics, medicine, chemistry, food industry, pharmaceutical industry, transport, vehicles, etc.) for its excellent chemical and physical properties. Unfortunately, UHMWPE, if submitted to high mechanical dynamical stresses, to high temperature and to high corrosive environment, it suffers alterations. Therefore, it is interesting to investigate the chemical and physical processes which can improve the UHMWPE wear resistance. Generally, the problem involves the polyethylene surface, and it need to be reinforced by the polymeric surface layers so that the friction wear can be reduced and the whole device lifetime increased [031]. An improvement of the wear resistance of UHMWPE can be obtained by using the LII induced by laser-generated plasma at high ion dose [030]. With this implanter, the ions are accelerated is directed toward a substrate at energies high enough to penetrate just below the substrate surface without causing damage to the lattice but modifying the target properties and improving the mechanical, thermal, electric and optical properties. In this investigation, a 99.99% pure carbon and a 99.99% titanium were used as the laser beam target, while the implanted substrate were three samples of polyethylene [030].

The above arguments described, are a summary of the studied investigations in this thesis. In particular have been examined more closely the study of the pulsed laser application in medical dentistry and the possibility to build a LII in order to induce ion implantation in different surfaces.
Introduction references


[026] [http://www.srim.org/](http://www.srim.org/)


1 Pulsed lasers

1.1 LASER GENERATED PLASMA. A THEORETIC MODEL

The study of the physical phenomenon that involve the interaction of high-powered laser pulses with targets placed in a vacuum chamber generates a fast evaporation, ionization of the ablated atoms and formation of a non-equilibrium plasma expanding from the target surface towards the external environment. In this model, the laser – generated plasma is treated as an ideal gas at high pressure and temperature, which is initially confined in small dimension, and is suddenly allowed to expand in vacuum. The forward-direction the laser evaporation process results from anisotropic expansion velocities of the atomic species which are controlled by the dimensions of the expanding plasma.
The nature of interaction of the laser beam with the target can be classified into three separate regimes: (i) interaction of the laser beam with the target, (ii) plasma formation, heating and initial three-dimensional isothermal expansion, and (iii) anisotropic adiabatic expansion. The first two processes occur during the time interval of the laser pulse, while the last process initiates after the laser pulse terminates. In these conditions, the evaporation of the target is assumed to be thermal, while the plasma expansion dynamics is non-thermal as a result of interaction of the laser beam with the evaporated material [1].

1.2 Interaction of laser beam with the target

Generally, the laser-solid interaction can be divided into two parts: (i) interaction of the laser beam with the target, and (ii) interaction of the laser beam with the evaporated material from the target material. The removal or sputtering of the material from the target, by laser irradiation, depends on the coupling of the beam with the solid. Intense heating of surface layers by high-powered laser pulses occurs, resulting in melting and/or evaporation of the surface layers depending on its energy density. Essentially, it involves the solution of the one-dimensional heat flow equation with appropriate boundary conditions taking into account the phase change in the material. The thermal history (heating rate, melting, evaporation) during pulsed-laser irradiation depends on the laser parameters (pulse energy density, pulse duration, wavelength), optical dependence of the temperature (reflectivity, absorption coefficient) and thermo-physical properties of the material (heat capacity, density, thermal conductivity, etc.). Fig. 1.1 shows a typical interaction of the laser beam with the target placed in vacuum chamber, at $10^{-7}$ mbar, with consequent plasma production.
Fig. 1.1 Typical laser-target interaction with plasma formation.

The energy deposited by the laser beam on the target is equal to the energy needed to vaporize the surface layers plus the conduction losses by the substrate vapour and the absorption losses by the plasma. The amount of laser power required to reach a surface temperature so high to produce significant vaporization is known as etching threshold. The value of the threshold depends mainly on the cohesive energy of the metal and on its thermal conduction. The lowest value of the etching threshold is found in sp-bonded metals, such as Cd and Pb, that they have a binding energy of about 3 eV. The transition metals and noble metals have intermediate binding energies of about 3-5 eV. While the refractory metals, such as Mo and W, have the highest binding energy (higher than 6 eV). A theoretical and approximate estimation of the energy threshold has been carried out using the following parameters [2]:

\[
\delta = \left( \frac{2}{\alpha \mu_0 \sigma} \right)^{1/2}
\]

(1.1)
where $\delta$ is the depth at which the intensity is reduced to 1/e of total, $\omega$ is the angular frequency of the used laser, $\mu_0$ is the vacuum permeability, and $\sigma$ is the electrical conductivity of the metal. This parameter is called *absorption depth*.

Another parameter is the *reflectivity*, $R$:

\[
R = \left[\frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}\right] = 1 - \left(\frac{8\omega\epsilon_0}{\sigma}\right)^{1/2}
\]

(1.2)

It is calculated for normal incidence, where $n$ and $k$ represent the real and the imaginary component of the complex refraction index, respectively, and $\epsilon_0$ is the vacuum dielectric constant.

Finally, with the classic ablative model proposed by Torrisi et al. [3], we have the energy threshold, i.e., the minimum energy required to evaporate the irradiated mass of the target,

\[
E_{\text{thr}} = \frac{m(c_s\Delta T + \lambda_f + \lambda_e)}{1 - R}
\]

(1.3)

where $m$ is the irradiate mass, $c_s$ is the specific heat, $\Delta T$ is the temperature rise, and $\lambda_f$ and $\lambda_e$ are the latent heats of fusion and evaporation processes, respectively. The irradiate mass is given of the following expression:

\[
m = \rho\left(\delta + \sqrt{D \cdot \tau}\right) \cdot S
\]

(1.4)
where \( \rho \) is the matter density, \( \delta \) the radiation depth penetration, \( D \) the thermal diffusivity and \( \tau \) is the laser pulse duration. Fig. 1.2 shows a comparison between the radiation depth penetration, \( \delta \), and the diffusion length, \( L = \sqrt{D \cdot \tau} \). The diffusion length is the maximum length inside the target where the heating, due to laser ablation, is felt respect to the target surface. In most cases here investigated, the absorption depth is negligible respect to the diffusion length.

\[ L = \sqrt{D \cdot \tau} \]

**Fig. 1.2.** Comparison between absorption depth and diffusion length.

In order to apply the relationship (1.4) to the biological tissue, the fig.(1.3.a) shows a numerical simulation of the diffusion length vs. pulse duration for different skin components. The thermal properties of tissue used in this preliminary study are listed in table (1.I) [140, 141].
The trend of the diffusion length increase with the width pulse, therefore in order to minimize the thermal damage, in an application medical of the laser, the duration of the pulse must be short.

![Diagram showing comparison between diffusion length and pulse duration for different skin components.](image)

**L = \sqrt{D \cdot \tau}**

Additionally, in fig. (1.3.b), the irradiated mass increases with the pulse duration of the laser, where the depth penetration is neglected respect to the diffusion length and the spot size is 1 mm².
Finally, the fig. (1.3.c) shows the temperature rise as a function of the laser energy. This simulation, has been performed using the latent heat of evaporation, $\lambda_e$, of the water because most of skin components are constituted of water (about 70%); while as a first approximation, the latent heat of fusion and the reflectivity have been neglected. The simulation shows as the temperature at the center of the laser spot grows quickly. Further investigations are reported in the third chapter of the present work.
In conclusion, we can say that the energy threshold, diffusion length, irradiated mass and temperature rise, depend on laser wavelength, pulse duration, and the thermal properties of the material. If the material parameters are independent of pulse energy density, a linear increase in evaporated material as a function of pulse energy density will be observed. However, a non-linear behavior, especially at high-energy densities, may be observed due to the change in plasma losses, reflectivity of the laser beam, and situations where the physical properties of tissue do not remain constant during laser radiation [4].

1.3 Interaction of laser beam with evaporated material
The high surface temperature induced by laser irradiation leads to emission of positive ions and electrons from a free surface. The flux of ions and electrons as a function of temperature can be predicted by the Richardson and Langmuir-Saha equations, respectively. Both of these equations show an exponential increase in the fraction of ionized
species with temperature. For a gas in local thermodynamic equilibrium (LTE) the fraction ionization can be theoretically calculated through the Saha equation, relatives to the ratio of single charged ions to neutrals in the plasma [5]:

$$\frac{N_i}{N_0} = 2.4 \cdot 10^{15} \frac{T^{3/2}}{n_e} e^{-I_0/kT}$$

(1.5)

where $T$ is the ion temperature in Kelvin units, $n_e$ is the electron density in cm$^{-3}$ and $I_0$ is the first ionization potential in eV. The exponential factor keeps the fraction ionization $N_i/N_t$ of the plume very small until the temperature is raised to where $I_0$ is only a few times $kT$. Then the fraction ionization rises suddenly and the vapor becomes a plasma.

Different mechanisms may play an important part in the ionization of the laser-generated species. Impact ionization, and other mechanisms, especially photo-ionization, thermal ionization of photon-activated species, and electronic excitation may affect the concentration of the excited species. In the Saha equation the fractional ionization is inversely proportional on the binding energy or melting point temperature. This indicates that the infrared laser irradiation produces mainly thermal effects in the target instead of photochemical ones. On the other side, the energy of single photons is not sufficient to induce ionization and to break chemical bonds; only free electrons can absorb it. In fact, electrons inside the interaction volume are accelerated in the laser radiation field by inverse bremsstrahlung until their kinetic energy is high enough to ionize the ambient gas or the material vapour; this increase the number of carriers by avalanche ionization. Thus, the plasma is the result of a macroscopic effect due to collective microscopic processes involving many electrons that, producing electron-electron and electron-atom collisions, give rise to multiple
ionization [6]. The material evaporated from the hot target is further heated by the absorption of the laser radiation.

The absorption primary occurs by an inverse bremsstrahlung process, which involves the absorption of a photon by a free electron. The absorption coefficient $\alpha_p$ of the plasma can be expressed as [1]

$$\alpha_p = 3.69 \cdot 10^8 \left(\frac{Z^3 n_i^2}{T^{0.5} \nu^3}\right) \left[1 - e^{-\left(\frac{h \nu}{kT}\right)}\right]$$

(1.6)

where $Z$, $n_i$, and $T$, are, respectively, the average charge, ion density, and temperature of the plasma, and $h$, $k$, and $\nu$ are the Planck constant, Boltzmann constant, and frequency of the laser light, respectively. The laser energy is highly absorbed if ($\alpha_pX$) is large, where $X$ is the dimension perpendicular to the target of expanding plasma. This equation shows that the absorption coefficient of the plasma is proportional to $n_i^2$. Thus, the plasma absorbs the incident laser radiation only at distances very close to the target where the densities of the charged particles are very high. In this equation the term $[1 - \exp(-h \nu/kT)]$ represents the losses due to stimulated emission, besides the plasma frequency is smaller than the frequency of the laser wavelength, otherwise, all the radiation would be reflected by the plasma.

As seem from Eq. (1.6), the heating of the evaporated material is controlled by the plasma absorption coefficient, which depends on the concentration of the ionized species, plasma temperature, wavelength, pulse duration, etc. The particle density in the plasma in turn depends on the degree of ionization, evaporation rate, and the plasma expansion velocities. Moreover, the absorption coefficient shows different temperature dependences for different energy density regimes.
It is reasonable to assume that during the duration of the laser pulse an isothermal temperature is attained near the target surface.

1.4 Adiabatic plasma expansion in vacuum

After the plasma formation and its initial isothermal expansion, during the incidence of the laser pulse, follows the adiabatic expansion of plasma in vacuum.

The adiabatic expansion of the plasma occurs where the temperature can be related to the dimensions of the plasma by the adiabatic thermodynamic equation given by

\[
T[X(t)Y(t)Z(t)]^{\gamma-1} = \text{const}
\]

(1.7)

where \( \gamma \) is the ratio of the specific heat capacities at constant pressure and volume, \( X(t), Y(t) \) and \( Z(t) \) are the dimensions of the expanding plasma in three orthogonal direction. The thermal energy is rapidly converted into kinetic energy, and the plasma attains an elevated expansion velocity. The rapid expansion of the plasma in vacuum results from large density gradients and large pressure gradients initially present near the outer edge (vacuum). In this conditions, of vacuum adiabatic expansion, the plasma temperature can be calculated by using the following relationship [5]:

\[
T = \frac{(\gamma - 1)^2}{\gamma} \cdot \frac{E}{2k}
\]

(1.8)

where \( \gamma \) is the adiabatic coefficient (\( \gamma = 5/3 \) for monatomic species), \( E \) is the average kinetic energy, and \( k \) is the Boltzmann constant.
The temperature decreases rapidly as the plasma expands; however, the drop is smaller at lower temperatures because energy is regained in the recombination of the ions.

The maximum attainable velocity for any gas in vacuum is given by [1]

\[ v = \frac{2v_s}{\gamma - 1} \]  

(1.9)

where \( v_s \) is the velocity of sound:

\[ v_s = \sqrt{\frac{\gamma RT}{m}} \]  

(1.10)

Thus, the maximum attainable velocity or asymptotic velocity is about 3-10 times the velocity of the sound, depending upon the value of \( \gamma \). In the adiabatic expansion regime, the velocity of the plasma increases due to a decrease in thermal energy of the plasma.

The equation of the gas dynamics which dictate the expansion of the plasma is the adiabatic equation of state

\[ \frac{1}{P} \left[ \frac{\partial P}{\partial t} + \vec{v} \cdot \nabla P \right] - \frac{\gamma}{n} \left[ \frac{\partial n}{\partial t} + \vec{v} \cdot \nabla n \right] = 0 \]  

(1.11)

and the equation of temperature

\[ \frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T = (1 - \gamma) T \nabla \cdot \vec{v} \]  

(1.12)

where \( P \) is the pressure into plasma, \( n \) the density, \( \gamma \) the specific heat capacity ratio, and \( \vec{v} \) the velocity that should be proportional to distance
from target [7]. If we presuppose that plasma behaves as a gas ideal, the pressure $P$, at any point in the plasma, is related to its density by the ideal gas equation

$$ P = nkT_0 $$

(1.13)

where $T_0$ is the isothermal temperature of the plasma and $k$ Boltzmann constant.

Furthermore we assumed that there are no spatial variations in the plasma temperature, or $\nabla T = 0$.

The solution which controls the expansion of the plasma in this regime is given by

$$ X(t) \left[ \frac{d^2 X}{dt^2} \right] = Y(t) \left[ \frac{d^2 Y}{dt^2} \right] = Z(t) \left[ \frac{d^2 Z}{dt^2} \right] = \frac{kT_0}{M} \left[ \frac{X_0 Y_0 Z_0}{X(t)Y(t)Z(t)} \right]^{\gamma-1} \quad t > \tau $$

(1.14)

where $X_0$, $Y_0$ and $Z_0$ are the initial orthogonal edges of the plasma after termination of the laser pulse ($t = \tau$). This equation shows that acceleration of plasma species depends upon the temperature and dimensions of the plasma, and the mass of the species. It should be noted that this hydrodynamic model is based on the equations of fluid flow, and the expansion velocities are controlled by pressure gradient in the plasma. Thus, this model applies to all species including atoms, ions, molecules, neutrals, small clusters, etc. However, based on the difference in their masses, the expansion velocities may be different for different species [1].

2. Knudsen – layer (KL). Outline

We consider here a pulsed beam of photons from laser that at time $t=0$ begins to strike the target surface and, as a result, the particles abruptly
begin to be released. If the release is thermal, the particle velocities will
be distributed as a Maxwellian \([8,9]\) characterized by number density \(n\),
pressure \(p\), temperature \(T\), positive velocities \((v_x)\) normal to the surface,
zero flow velocity \(u\), and zero Mach number \(M\).

For emission at low number densities, the particle disperse without
collision and the velocity distribution function has the form of a “half-
range” Maxwellian, i.e. the velocities normal to the surface take on
only positive values \([9,10,11]\), furthermore the angular distribution
shows to have the approximate form \(\cos \theta\), and there is no
recondensation at the surface.

This velocity distribution function, \(f^+_s\), so-called “half-range”
Maxwellian \([12]\), has the form:

\[
\begin{align*}
    f^+_s(v_x, v_y, v_z, E_i) &\propto \exp\left\{-\frac{2E_i + m(v_x^2 + v_y^2 + v_z^2)}{2kT_s}\right\} \\
    v_x &\geq 0, \quad -\infty < v_y < \infty, \quad -\infty < v_z < \infty.
\end{align*}
\]

(1.15)

Where \(v_i\) \((i=x,y,z)\) are the velocity component, \(E_i\) is the total internal
energy (is somewhat an idealization that serves to insure that the result
is thermodynamically correct), \(m\) is the mass of the particles, \(k\) the
Boltzmann constant, and \(T_s\) is the surface temperature. The average
velocity \(v_x\) in eq. (1.15) is:

\[
\langle v_x \rangle = \left(\frac{2k_B T_s}{\pi n m}\right)^{1/2}
\]

(1.16)

and can be regarded as a sort of center-of-mass velocity, called flow
velocity.
At higher number densities, collisions occur with the result that negative values of $v_x$ develop and the situation could be describe in terms of the particles replacing their original implicit center-of-mass velocity with an explicit center-of-mass velocity, $u_k$. This lead to an altered velocity distribution function which is commonly approximated as a “full-range” Maxwellian [12] incorporating the explicit center-of-mass velocity, $u_k$. The resulting distribution function is:

$$f_k^+ \propto \exp \left\{ - \frac{2E_f + m(v_x - u_k)^2 + v_y^2 + v_z^2)}{2kT_k} \right\}$$

$$-\infty < v_x, v_y, v_z < \infty$$

(1.17)

The velocity $u_k$ in eq.(1.17) was shown to be similar to the velocity of sound, given approximately by:

$$u_k = a_{\text{sound}} = \left( \frac{\gamma kT_k}{m} \right)^{1/2}$$

(1.18)

where $\gamma$ is the heat capacity ratio, $k$ the Boltzmann constant, and $T_k$ is the temperature at the Knudsen layer boundary.

$T_K$ was shown to be about 70% of $T_s$ for monatomic species [9,10,11]. An estimate of the surface temperature, $T_s$, has been done into work of Kelly and Dreyfus [12] in which time-of-flight (TOF) measurements are made to know the energy, $\hat{E}$, defined by the peak position of the TOF spectrum and related to surface temperature, $T_s$, by the relation:

$$kT_s = \frac{\hat{E}}{\eta_k}$$
with $\eta_k$ ranging from 2.52 for monatomic species to 3.28 for a species with many accessible internal degrees of freedom [12].

The distribution function of eq. (1.17) shows strong forward peaking, $\sim \cos^4 \theta$ [13], and leads to significant recondensation. Therefore, we will use the term *Knudsen layer* [10,11,9,14,15] to describe the region within a few mean free path of the target surface in which the change from eq. (1.15) to (1.17) occurs as a highly non-equilibrium collision process [12].

Still further collisions occur, leading to the well-known phenomenon of the adiabatic expansion, which is described by a relation similar to eq. (1.17) but with $u_K$ exceeding the velocity of sound and the temperature being less than $T_k$ [16].

A further important aspect of KL formation is that a significant fraction of the emitted particles is scattered back towards the target surface [9]. In fig (1.4.a) we have a schematic representation of KL formation [20].

![Fig. 1.4.a. Schematic representation of KL formation followed by free flight. The gas nearest the surface is characterized by $v_x > 0$ and $u = 0$, while at the KL boundary the gas shows $-\infty < v_x < +\infty$ and $u = u_K$. The particles finally go into free flight.](image)

For larger quantities of particles, an *unsteady adiabatic expansion* (UAE) occurs governed by eqs. below reported [17,18]:
Here $u$ is flow velocity (the flow is assumed to be one-dimensional), $\gamma = C_p / C_v$ is the heat capacity ratio, $\rho$ is the particle density, $p$ is the pressure, $E_i$ is the internal energy per unit mass and $\Phi$ (in the case of laser-pulse bombardment) is the laser heat input into the escaping particles in units $\text{J/cm}^2\text{s}$.

In addition, we introduce the equation of state of a perfect gas,

$$
p = n k_B T = \rho k_B T / m = \rho a_s^2 / \gamma
$$

(1.23)

and the condition for the adiabatic, reversible isentropic expansion of a perfect gas that connects the density to the speed of sound by the relation [19],

$$
\rho \propto a_s^{2/(\lambda - 1)}
$$

(1.24)
The result is that the flow velocity increases beyond $u_k$; $a_{\text{sound}}$ decreases below $u_k$, and there is a more marked forward peaking as determined by $M = u/a (\cos^8 \theta$ to $\cos^3 \theta)$. This is schematized in fig (1.4.b) [20].

Fig. 1.4.b. Schematic representation of a KL followed by an *unsteady adiabatic expansion* (UEA). In this condition the number of collisions is more than that necessary for KL formation, so that with increasing distance the gas kinetic velocities decrease and at same time $u$ increase beyond $u_k$. The particles finally go into free flight but is not shown.
2 Measurements concerning the characterization of laser-produced plasmas

2.1 Measurements on ions

This chapter is dedicated to the corpuscular diagnostic from laser-emitted plasma. This diagnostic gives information about the plasma parameters at long distances from the target. During the high power laser interaction, a part of the absorbed energy is released to the emitted atoms, clusters, ions and electrons and another part is released to the emitted energetic photons (IR, visible, UV and X-ray). The ion distribution, the total number of ions, their average and maximum charge states, the abundance of ion species and energy carried by them gives very precise information about the mechanisms of the laser interaction with the matter.

The principle of operation described in this paragraph is based on the time-of-flight (TOF) method. This means that the measurement of ion velocity consists in measuring the time of flight, $t$, of the ions passing the distance $L$ from the plasma focus to the detector. The time-of-flight method is correct in the case when $t \gg \tau$ and $L \gg r$ (where $\tau$ is the laser pulse duration (ns) and $r$ is the radius of the laser focus spot, $\sim$1mm). The corpuscular diagnostics based on the time-of-flight method treat the laser-produced plasma as a point source of ions [21].
Analyzers are used to determine the ion energy spectra and the abundance of ion species in the plasma. Because the expanding plasma is, in principle, quasi-neutral, the separation of plasma into ion and electron components must be performed and the electron component should be removed completely. With the considerations of Woryna et al. (1996) we have the result that, in the case of adiabatic spherical expansion, the condition for plasma separation in ion analyzers will be in the following form:

\[
U / \Delta R >> 4\pi e n_i b_{in}
\]  

(2.1)

where \(U\) and \(\Delta R\) are the voltage and the spacing between the plate of the analyzing system, respectively, \(e\) is the electron charge, \(n_i\) is the ion concentration with the charge state \(z\), and \(b_{in}\) is the width of the entrance slit of the analyzer.

Because the ion current densities (mA/cm\(^2\)) at long distances from the target makes a charge space effects that influences the energy resolution of the ion particle analyzer, Green (1970) gave the condition limiting the usable plasma density \(n_i(L)\) (cm\(^{-3}\)) for which space charge effects could be neglected (for only ion beams),

\[
n_i \leq 5 \cdot 10^8 \frac{E}{l^2} \frac{b_{out}}{z b_{in}}
\]

(2.2)

where \(b_{out}/b_{in}\) is the ratio of the entrance-to-output width of the analyzer, \(E\) is the energy of ions with the charge state \(z\), and \(l\) is the path of flight of ions inside the analyzing system [22].

The electrostatic cylindrical ion energy analyzer (IEA) is a mass spectrometric combined with the time-of-flight method for the diagnostic of ion source and, in particular, for measurement of generated plasmas from the laser.
In fig. (2.1), we have a schematic drawing of the main part of the IEA, i.e. the deflection system.

![Fig. 2.1. Scheme of the deflection system of the cylindrical electrostatic IEA. $R_1$, inner plates; $R_2$, outer plates; $\Delta R$, mean radius; $|V_2| = V_1 = U/2$, potential of the deflection plates; $b_{\text{in}}$, $b_{\text{out}}$ width of the input and output slits, respectively; $\psi$, deflection angle; WEM (windows electron multiplier), detector; $T$, target.](image)

It is made of two coaxial metallic cylinders of radii $R_1$ (inner plate) and $R_2$ (outer plate) maintained at potentials $V_1$ and $V_2$ with a symmetric polarization, $V_2 = -V_1 = U/2$, respectively, and with deflection angle, $\psi$, at 90 degrees. The radial electric field, at the centre of the deflection system, on the radius of the equipotential surface is given by

$$E_r = \frac{(V_2 - V_1)}{r \ln \left( \frac{R_2}{R_1} \right)}$$

(2.3)

where $r$ is the radius of an equipotential surface and $R_1 \leq r \leq R_2$. The equipotential surface $V_0 = 0$ exists for
\[ r = R_0 = (R_1 R_2)^{1/2} \approx \frac{(R_1 + R_2)}{2} \]

(2.4)

when \( R_0 \) is the mean radius of the deflection plates.

Under these conditions, a particle with the charge \( ez \), mass \( m \), and velocity \( v \) is detected only if its kinetic energy \( E \) satisfies the following expression:

\[
\frac{E}{z} = \frac{eU}{2 \ln \left( \frac{R_2}{R_1} \right)} \equiv \kappa eU
\]

(2.5)

where \( \kappa = \frac{R_0}{2 \Delta R} \) is the geometric factor of the IEA, with \( \Delta R = R_2 - R_1 \) the spacing between the deflection plates of the analyzing system, \( e \) the elementary charge, and \( U \) the voltage on the plates. By changing the \( U \) bias it is possible to detect different \( E/z \) ratios.

From eq. (2.5) we have that the IEA is operated as an energy filter as only ions with a given energy-to-charge state ratio can pass through the IEA and reach the detector.

The resolving power, of the electrostatic analyzer in discussion, is given by

\[ R_m = \frac{t}{(2\Delta t)} \]

(2.6)

where \( t \) is the time of flight of an ion, and \( \Delta t \) is the time distance between the resolved ion pulses, as shown in fig. (2.2).
Its mass resolution, $R_m = \frac{m}{\Delta m}$, has been determined experimentally and it results to be about 150 [23].

For the measure of time flight, together to IEA, we have need of an ions collector. A simple ion collector scheme is reported in fig. (2.3).

It consists of a little Faraday cup with an inner grid connected to the ground. The collector is biased to a negative voltage $V_c$ (-100 V usually). The ion current, measured at the time $t$, is given by
\[ I_c(t) = \frac{V_c(t)}{\varepsilon \cdot R_{load} \left( 1 + \frac{\sigma(t)}{z(t)} \right)} \]

(2.7)

where \( \varepsilon \) is the transparency of the grid (58 \%), \( R_{load} \) is the load resistance (25 \( \Omega \)), \( \sigma(t) \) represents the mean secondary ion-electron emission coefficient, and \( z(t) \) is the mean charge state of the ions. For the range of the ion energy and the ion charge state found in our experiment, the \( \sigma(t)/z(t) \) ratio can be approximated to one [24].

The ion collector output is connected to a 500 MHz memory oscilloscope, showing a \( mV \) signal as a function of the time flight. A typical ion collector signal is shown in fig. (2.4) [25].

![Typical ion collector signal](image)

**Fig. 2.4.** Typical ion collector, showing a very fast photopeak employed as a start signal for time-of-flight measurements.

This spectra show on their left-hand side a very fast photo-peak which is employed as a start signal for TOF measurements. The photo-peak is due to collector current of the electrons emission for photoelectric effect caused by incident laser photons. This peak is almost contemporaneous.
to the laser impulse and represents the start signal for measurement of flight timing. On right-hand side it shows a broader peak due to the total ions detection, it permits us to measure the average time-of-flight of the ions ejected from the surface and to calculate their average velocity and average kinetic energy through the known target-collector distance (60 cm, in our case). In fig. (2.4) we have ions tantalum with single charge state whit time-of-flight measured of 19 µs and average velocity and average kinetic energy calculated of $3.16 \times 10^4$ m/s and 936 eV, respectively.

In order to have information about the ion charge state, in fig. (2.5) it is reported a typical IEA spectrum together IC signal as a function of the acquisition time reporting different charge states of the Ta ions [26].

![Fig. 2.5. Typical IEA spectrum together IC signal.](image)

The spectra show the start peak at left-hand side (the photo-peak) and the negative peaks at the right-hand side that show the time of arrival of the ions to a WEM. Each negative peak represents ions with a given value of the $E/z$ ratio. In this case the $E/z$ ration ranges between 565 eV for charge state $z=1$ up to 4520 eV for charge state $z=8$, by using 50 V
bias voltage for deflection plates and a geometric factor of 11.3. The TOF between the start and the negative peak allows us of to calculate, knowing the target-collector distance, the velocity and the energy of the ions [26]. By changing step-by-step the bias voltage $U$ (ranging from ±10 up to ±120 V), it is possible to detect ions having different $E/z$ ratio and so to determine the experimental ion energy distribution as a function of the ion charge state.

Fig. (2.6) shows a typical examples of the ion energy distribution for tantalum ions, obtained by using a high laser fluence (100 J/cm$^2$), as a function of their charge state [26].

![Fig. 2.6. Typical ion energy distribution for Ta ions as a function of the charge state at high laser fluence (100 J/cm$^2$).](image)

In these distributions, eight charge states (from Ta$^{1+}$ up to Ta$^{8+}$) are detected and plotted. They give important information about mechanisms of the plasma formation, and to evaluate the thermal and the Coulomb contributions to the ion energy distribution. The mono-charged ions show almost Maxwellian energy distribution while ions with higher charge states have a different distribution whose peak value is shifted towards higher velocities. This result, in agreement with the
literature [27, 28], introduces a “flow velocity” to describe the velocity of the centre of mass of the expanding plasma.

The ion energy distribution shown in fig. (2.6) can be fitted by a “shifted Maxwellian distribution”, where at long distance from the target, the velocity distribution is given by the following function [27, 29]:

\[
F(v_x) = \left( \frac{m}{2\pi kT} \right)^{3/2} v_x^3 \cdot e^{-\frac{m(v_x-u_k)^2}{2kT}}
\]

(2.8)

where \( v_x \) is the gas kinetic velocity, with normal direction to the target surface, which follows a Maxwell distribution in the region where collision occur (Knudsen layer) [28]; \( u_k \) is the so-called “flow velocity” indicating the plasma centre-of-mass velocity along the normal to the target surface due to the gas expansion; \( m \) the ion mass; \( T \) is the temperature of the plasma; \( k \) the Boltzmann constant.

The shape of the experimental ion-energy distribution, permits us to evaluate the mean ion energy and the mean ion velocity for each charge state. Observing the fig. (2.6) it sees itself that the mean energy of Ta\(^{1+}\) is about 1000 eV corresponding to \( 3.16 \times 10^4 \) m/s velocity, while for Ta\(^{8+}\) is about 5.2 keV corresponding to \( 7.1 \times 10^4 \) m/s velocity. The experimental measurements demonstrate that the ion energy increases about 600 eV for charge state, so it is plausible to suppose that ions inside the plasma are submitted to an electrical Coulomb acceleration. In order to consider the Coulomb effects inside the plasma, the “shifted Maxwellian distribution” is replaced by a better fit of the ion-energy distribution through the following relationship:
\[
F(v_x, v_c) = A \left( \frac{m}{2\pi kT} \right)^{3/2} v_x^3 \cdot e^{-\frac{m(v_x-u_k-u_c)^2}{2kT}}
\]

(2.9)
called “\textit{shifted Maxwellian-Coulomb distribution}” [26].

In this relationship, \(A\) is a constant of normalization to the experimental data; \(v_x\) the mean thermal velocity of neutrals (isotropic distributed), with analytical relationship:

\[
v_x = \sqrt{\frac{3kT}{m}}
\]

(2.10)
where \(k\) is the Boltzmann constant, \(T\) the temperature and \(m\) the mass of the ionic kind in question; \(u_k\) is the velocity of the plasma expansion in vacuum, along the target-normal, and according to the adiabatic expansion model given from the following relationship:

\[
u_k = \sqrt{\frac{\gamma kT}{m}}
\]

(2.11)
where \(\gamma\) is the adiabatic coefficient (\(\gamma = 1.67\) for monatomic species).

The sum of these two velocities, \(v_x + u_k\), due to thermal processes, occurs along the x-axis (i.e. along the normal to the target surface).

Finally, \(u_c\) is the velocity of the ions due to the Coulomb acceleration. It depends on the equivalent voltage, \(V_0\), according to the classical model:

\[
u_c = \sqrt{\frac{2ezV_0}{m}}
\]

(2.12)
where $e$ is the electron charge, $z$ is the charge state. The equivalent accelerating voltage, $V_0$, is developed inside the non-equilibrium plasma because of the increase of the charge state that shifted the distributions towards high energy. Since the shift is a linear function of the laser fluence and that in our experiment it ranges between 50 eV and 85 eV, we can assume that inside the non-equilibrium plasma it is generated an equivalent acceleration voltage, $V_0$, ranging between 50 V up to 85 V [30].

Converting the eq. (2.9) in terms of energy distribution, permits us to fit the experimental ion energy distribution of fig. (2.6) and to extrapolate a better $A$, $T$, $u_k$, and $u_c$ values. Besides, since the comparison between the theoretic relationship of the eq. (2.9) and the experimental fit of the fig. (2.6) is good, the eq. (2.9) can be used both as a fit function of the experimental data and as a simulation function for future prediction. As a result of this, are shown the fits of two ion energy distribution with charge state of 1+ and 8+, respectively, using the MATLAB code [31]:

The two fits are obtained with temperatures $T$ of 2.80 and $4.30 \times 10^6 \, ^\circ K$ and with fit velocities $v_{fit}$ of 2.80 and $6.40 \times 10^4 \, m/s$, respectively. The fit velocity is the sum of $u_k$ and $u_c$. The relative $A$ intensities are 94% and 31%, respectively, and the different values can be explained on the basic
of different ionization cross-sections and of the recombination probabilities of ions and electrons inside the plasma [26].

Finally, the fig. (2.8) shows the simulation functions for tantalum irradiation at high laser pulsed energy, which are very similar to those experimentally obtained and reported in previous fig. (2.6) [26, 31].

![Graph showing ion-energy distributions for different charge states of Ta ions.](image)

Fig. 2.8. Simulations of the ion-energy distributions for different charge state of Ta ions obtained by the shifted Maxwellian-Coulomb function at high laser fluence.

The good agreement allows us to separate the contribution to the total ion energy coming separately from neutral and from ionized atoms and from thermal and Coulomb interactions.

More details about the main parameters to fit the ion-energy distribution by using the “shifted Maxwellian-Coulomb distribution” are reported in [26].
2.2 Measurements of electrons by pulsed-laser ablation

The measurement of the electrons emission from plasma produced by laser ablation it is another method of understanding of the plasma generation and of the interaction of the radiation with the mater. The theoretical aspect of the problem has been discussed in chapter one, while here we will discuss the experimental aspect. The main instrument employed for the measurements of the energetic electrons (hot electrons or primary) ejected during the laser-pulse ablation, has been a little Faraday cup. It was placed at different angles with respect to the normal to target surface and different distances from the target. A typical scheme of a little Faraday cup is represented in fig. (2.3). A collector plate was polarized -50 Volt for positive ions detection, and +50 Volt for electrons detection. The output signal of the Faraday cup was detected through a 50 Ω load resistance, everything connected to a fast storage oscilloscope.

In this experiment, have been irradiates targets of Tantalum and Copper, respectively. As first result, shown in fig. (2.9.a), we have that the ion emission yield from Ta and Cu versus laser intensity, respectively,

![Graph showing emission yield of Ta and Cu versus laser intensity for ions.](image-url)
are higher with respect to the primary electron yield, shown in fig. (2.9.b).

Fig. (2.9.b). Emission yield of Ta and Cu versus laser intensity for primary electrons.

In fact, the fast electrons have a yield of about four orders of magnitude lower with respect to the yield of ions [32]. Instead, in fig. (2.9.c), the secondary electron yield is about a factor of 100 higher with respect to the yield of ion.

Fig. (2.9.c). Emission yield of Ta and Cu versus laser intensity for secondary electrons.
These results can be explained on the basis of the measures of the potential induced by the laser ablation on an insulated target during and after the laser interaction. At this purpose, the fig. (2.10) shows the target charge as a function of time for Ta and Cu, respectively.

Fig. 2.10. Target charge as a function of time for Ta and Cu.

Results indicate that during the laser irradiation, the target is positively charged due to a fast electron emission. This charge reaches a maximum value (depending on the laser pulse intensity) at a time of \( \sim 100 \) ns from the laser shot after which it decrease exponentially to reach a small negative values (at \( \sim 600 \) ns) due to slow emitted electrons that are backscattered on the target. Only after \( \sim 1-2 \) ms, the target charge tends to zero. These results demonstrate that during the laser irradiation, the fast electrons go away from the target, producing a positive charge on it. The plasma generated in front of the target produces electron emission but the positive potential of the target, \( \sim 20-30 \) V, become sufficient to force the ejected secondary electrons to come back to the target,
producing a reduction in the positive voltage and permitting to the target to reach a negative voltage of the order 1 V. In these conditions the fast electrons should be emitted only during the time of laser pulse irradiation or immediately after, demonstrating that the emission is due only to few electrons escaping from the negative cloud potential at the target surface.

The secondary electron emission occurs for longer times producing low electron energies but in number higher with respect to the number ions. This difference is reduced for measurements performed near to the target surface at which a quasi-neutrality charge of the plasma occurs. At large distance, instead, the ion yield is reduced. Such results indicate that plasma emitted from the target surface contains ions, electrons and neutrals [32].

Finally, the measured fast-electron kinetic energies, ~2-3 keV, have been in agreement with the literature data [33] and with X-ray measurement performed at LNS, demonstrating that X-ray energy of ~2-3 keV can be produced by plasma-laser as a process of primary electron bremsstrahlung effect [34], as will be shown later on.

2.3 Measurement on neutrals

The plasma produced for interaction of energetic laser pulses with the matter contains, in addition to ions and electrons, also neutral species as atoms, molecules and clusters. The role of the neutrals is very important in the cases of the laser ion source (LIS) application and pulsed-laser deposition (PLD) technique [118, 119]. For instance, PLD permits to obtain high adhesion of thin films on substrate because of the neutrals’ energy that have an order of magnitude higher with respect to the energy of only evaporative component. Furthermore, the neutrals with
high energy can be implanted in the first superficial layers of a substrate [119].

In the LIS application, the neutrals can be to inject in ion sources to be ionized by microwaves in electron-cyclotron resonance (ECR) and successively extracted to produce high current beams for the accelerators [118].

The role of the neutral species is very interesting, especially in the low laser intensity regime at which the neutrals’ production is high. The atomic neutral emission, in fact, is relevant at low intensity of the laser pulse just above the ablation threshold value, at which vaporization processes are predominant with respect to ionization ones. At high laser intensity, the ionization cross-section increases and high charge states are produced as a result of energetic electrons interacting with neutrals and ions [47]. At this regimes, the presence of neutrals decreases significantly.

The velocity of the neutrals is performed using a special mass quadrupole spectrometer (MQS) which ionizes neutrals and measures their energy through electrostatic deflection.

The fig. (2.11) shows four typical MSQ spectra, two relative to the tantalum ablation at energy laser of 100 mJ and 5 mJ, respectively, and two relative to the aluminium ablation at same energy laser of tantalum target [48]. A Nd: YAG laser with a visible light (532 nm) and an intensity of the order of $10^9$ W/cm$^2$ has been employed for this investigation.
Fig. 2.11. Typical MSQ spectra relative to the tantalum ablation (a) and (b) and aluminium ablation (c) and (d).

The spectra represent the energy distribution of the neutral’s emission yield versus neutrals’ energy. The various peaks observed in this figure are due to the different values of the neutrals’ temperature into plasma and shows that the average energy of the neutrals increases with the pulse intensity. Therefore, the peaks obtained at low laser pulse energy are due to the plasma’s cold neutrals, while the peaks obtained at high laser pulse are due to the hot neutrals of the plasma’s core.

Theoretically, the plasma neutrals’ temperatures T (eV) have been calculated assuming a Local Thermal Equilibrium (LTE) by using the relation

$$kT = \frac{m \nu^2}{3}$$

(2.13)

where $m$ is the ion mass, $\nu$ the ion velocity, and $k$ the Boltzmann constant. The $\nu$ was measured through the IEA.
This temperature follows the neutrals’ average energy trend and it reaches a maximum value of $\sim 75$ and 50 eV for tantalum and aluminium, respectively [48].

The fig. (2.12) shows a comparison between plasma neutral’s temperature measured with MSQ and ion’s temperature obtained with TOF measurement versus laser energy [41].

Fig. 2.12. Temperatures comparison among ions and neutrals versus laser energy.

The differences between ion’s temperature and neutral’s temperature are due to electrical field inside the plasma that accelerates the ions but does not influence the neutrals. This difference, in fact, is more marked for high energies because of high charge states. Finally, for a study more deepened, the recombination mechanism must be taken in consideration for the generation of energetic neutrals.
2.4 Measure of the X-ray emission from plasma obtained by laser ablation

The interest for the X-ray emission from laser-generated plasma is high because it finds many applications in a range of scientific fields, such as medicine, biology, chemistry and engineering [35, 36]. We already know that the interaction of energetic laser pulses with solid targets produces fast evaporation, excitation and ionization of the ejected particles. Photons, electrons, ions, neutrals and clusters are ejected energetically from the plasma that it has formed itself. Depending on the laser intensity, visible, ultraviolet, soft and hard X-ray can be, also, produced by the plasma. These emissions are due to de-excitation processes, ion recombination effects and electromagnetic radiation (Bremmstrahlung) inside the plasma. At the laser power density of more than $10^{10}$ W/cm$^2$ the plasma makes a source of very intense radiations [37]. The analysis of the photon emission, both for the continuum and the characteristic lines, permits to characterise the laser-generated plasma in terms of temperature, charge state, fraction ionization, density and spatial-temporal evolution of the plasma. In this section, the pulsed plasma produced by ns laser is investigated in the visible region and in the range of soft X-ray emission [38].

The used detector type for the X-ray emission measure has been a bi-planar soft-X-ray (vacuum) diode (SXRD). A scheme of the SXRD detector is sketched in fig. (2.13), where it sees itself that the photons pass through a mesh and strike the photocathode. The output signal of the detector, with opportune bias, is measured with the use of a storage oscilloscope.

In order to filter the detection radiation, thin Mylar films of different thickness ($0.2$ µm $\div$ $2$ µm) were used as soft X-ray absorbers in front of
SXRD, where the Mylar is a polyester film of $(C_{10}H_8O_4)_n$ composition with a density of 1.01 g/cm$^3$.

Fig. 2.13. Scheme of the SXRD detector.

Fig. (2.14) shows the results of measurements of X-ray yield as a function of the laser wavelength and laser energy for Cu target.

Fig. 2.14. X-ray yield produced by Ta plasma as a function of the laser pulse energy at 1064 nm and 532 nm wavelength.
The plot indicates that the X-ray yield at IR irradiation is higher with respect to that produced by visible radiation employed in the same experimental conditions and that there is a fast increase of the yield as soon as the laser energy increases [38].

A measurement of X-ray obtained from a single laser shot as a function of different Mylar films thickness permits to plot the relative yield measured in terms of transmitted ($I_T$) to incident ($I_0$) intensities ratio, $I_T/I_0$, versus Mylar thickness. This allows to obtained the average absorption coefficient value of the X-ray spectrum by using the absorption exponential law

$$\frac{I_T}{I_0} = e^{-\mu \cdot x}$$

(2.14)

where $\mu$ is the absorption coefficient and $x$ the Mylar thickness. Fig. (2.15) shows the transmission curve of the mylar vs. the X-ray energy for three different absorber thicknesses, where the transmission is defined as the fraction of radiation energy that passes through a filter.
Fig. 2.15. Mylar transmission as a function of the photon energy for different absorbed thickness.

Fig. (2.16) shows the results obtained from Ta target irradiation at two wavelengths.

By using the extrapolated absorptions coefficients, through the transmission data reported in literature \cite{38}, it is possible calculate, in first approximation, the average energy, $\bar{E}$, of the X-ray collected by the detection system. The calculations have given the result of $\bar{E} = 300$ eV for laser shot operating at 532 nm and $\bar{E} = 350$ eV for laser shot operating at 1064 nm. The values obtained are somewhat higher than the energy of maximal sensitivity of the detector (250 eV), this means that the SXRD detector capture harder X-rays and, therefore, we can say that the X-ray spectrum contain soft X-rays with energy below 50 eV,
and hard X-rays with a tail energy of the order of 300 ÷ 350 eV, in agreement with previous data [39]. Similar average energies were obtained irradiating Al and Cu. Furthermore, measurements indicate that the X-ray yield coming from different targets decreases going from copper to aluminium and to tantalum. Probably this result is due to the decrease free electron density from Cu to Al and to Ta. The free electrons that absorb energy by the photons, can be ejected from metal and subject, in the plasma, at radiative losses (bremsstrahlung) that take the form of soft X-ray [38].

2.5 Temperature of laser-generated plasmas

In this section a special attention it is put on one of the parameters of the plasma, i.e. the temperature. The temperature of the plasma is a parameter strongly dependent on the collision among ions, electrons, and the neutrals. Moreover, the temperature is strongly dependent on the duration time just after the laser pulse and on the distance from the surface of irradiated target [33, 40].

To consider the temperature of the plasma, the measurements of the energy, velocity, and other physical parameters of the particles that constitute the plasma they are necessary. With the use of an IEA (Ion Energy Analyzer), in fact, is possible to measure the E/Z ratio and to elaborate the experimental data in terms of ion energy distribution as a function of the charge states. As seen in section 2.1, the experimental data can be fitted by following the “shifted Maxwellian-Coulomb distribution” from which it is possible to evaluate the average temperature of the ions. In fig. (2.17) it is reported the calculated ion temperature obtained with experimental ion energy distribution data fit as a function of the charge state [41].
The denoted curve with $Te$ (Chen et al) shows the electron temperature calculated through the relation:

$$kT_e = \frac{m_i v_i^2}{\langle z \rangle}$$

(2.15)

with that Chen [42] demonstrates that the electronic plasma temperature is usually higher than the ion temperature. In the relation (2.15), $m_i$ is the ion mass, $v_i$ the ion velocity, $k$ the Boltzmann constant, and $\langle z \rangle$ the average charge state. In this case, the electrons temperatures decrease while increase the average charge state.

With the $Te$ (Fyan et al) curve, Fyan uses the same semi-empirical approach of Chen but decrease the estimation to 62% for a better interpretation of the experimental measurement. The relation that shows the trend in figure is:
\[ kT_e = \frac{5m_i v_i^2}{8\langle z \rangle} \]

(2.16)

Finally, Morse and Niels [43] have shown that the temperature of the hot electrons can be estimated by the following relation:

\[ kT_e = \frac{\langle E_f \rangle}{1.25\langle z_f \rangle} \]

(2.17)

where \( E_f \) and \( \langle z_f \rangle \) are the mean energy and the mean charge state of fast ions, respectively, where the ions are accelerated in the electrostatic potential created by the hot electrons.

The curve labelled \( Ti \) (Torrisi-PALS) represents another approach that was used to calculate the ion temperature by extrapolating the experimental ion energy distribution with a fit by using equation (2.9) [41, 44], while in the curve labelled \( Ti \) (Torrisi-LNS) the ion temperature was calculated by considering thermal motions of ions. In this thermodynamic model, the relation that joins the thermal motions of ions with their velocity is:

\[ kT_i = \frac{m_i v_i^2}{3} \]

(2.18)

where \( m_i \) is the ion mass, \( v_i \) the ion velocity, and \( k \) the Boltzmann constant. The \( v_i \) was measured through the IEA.

Furthermore, the fig. (2.17) [41] shows a comparison between ion and electron temperatures, as a function of the charge state, indicating
that, in general, the temperature increases linearly with the charge state as shown the following empirical expression:

\[ kT = A z \]  

(2.19)

where \( A \) is the fit parameter and \( z \) is the charge state.

These data demonstrate that the electron temperature is higher with respect to the ion temperature [41]. At higher charge states the thermal model is not acceptable because need consider the greater contribution of the electrical field on the acceleration of the ions [44].

In case of plasma in local thermal equilibrium (LTE) the electronic temperature can be determined using the following relation [45]:

\[ N_e (cm^{-3}) \geq 1.4 \times 10^{14} T^{1/2} (eV) [\Delta E (eV)]^3 \]  

(2.20)

where \( T \) is the plasma temperature and \( \Delta E \) is the energy difference between the states which expected to be in LTE conditions. Nevertheless, a theoretical prediction accredited for hot electrons temperature is given by following empirical relationship [37, 120]

\[ T_e (keV) = 6 \times 10^{-5} \left[ I (W/cm^2) \lambda (\mu m)^2 \right]^{1/3} \]  

(2.21)

where \( I \) is the laser intensity and \( \lambda \) is the photon wavelength.

In a typical experiment of carbon-plasma obtained by a Nd:YAG laser operating at 532 nm with 3 ns pulse duration (Gaussian beam profile), the eq. (2.21) gives a temperature values of 49 eV with a maximum laser pulse energy of 170 mJ and a spot size, on the target, of 3 mm² [30].

Another method of estimation of the electron temperature can be obtained from optical spectrum observation. In fig. (2.18) we have a typical optical spectrum obtained irradiating target titanium in vacuum
at 270 mJ with a Nd:YAG pulsed laser operating at 1064 nm wavelength with 9 ns pulse width [122].

Fig. 2.18. Optical spectroscopy spectrum into range 200-800 nm wavelength, detecting the visible radiation emitted from the Ti laser-generated plasma, at 270 mJ pulse energy.

A linear fit of experimental data is used by employing the Boltzmann plot method that puts in connection the estimate excitation temperature distribution, in the plasma, with the emission intensity of a line. If, in fact, the plasma is in local thermal equilibrium (LTE), the population of the excited state can be estimate with the Boltzmann distribution as following [46]:

\[ n_{ik} = n_i \frac{g_k}{Z} e^{-E_k/kT} \]  

(2.22)

where \( n_{ik} \) is the population of the k-th excited level; \( g_k \) the statistical weight of the upper level of the transition; \( E_k \) the excitation energy; \( k \) the Boltzmann’s constant; \( T \) the temperature and \( Z \) the partition
function. The emission intensity of a line is related to the population of the excited level through the following relation [46]:

\[
I_{ik} \approx A_{ik} n_{ik} \frac{hc}{\lambda_{ik}} = A_{ik} n_i \frac{g_k hc}{Z\lambda_{ik}} e^{-E_k / kT}
\]

(2.23)

where \(A_{ik}\) is the atomic transition probability and \(\lambda_{ik}\) is the wavelength of the line. The data of the values assumed by the atomic transition probabilities \((A_{ik})\), statistical weights of the upper levels of the transition \((g_k)\), excitation energy \((E_k)\), relative emission intensity \((I_{ik})\) and emission wavelength \((\lambda_{ik})\) for the visible region [121] are reported in table (2.1).

<table>
<thead>
<tr>
<th>(\lambda_{ik}) (nm)</th>
<th>(A_{ik} \times 10^8) (s(^{-1}))</th>
<th>(g_k)</th>
<th>(E_k) (eV)</th>
<th>(I_{ik}) (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutrals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>365</td>
<td>0.058</td>
<td>7</td>
<td>3.4</td>
<td>54</td>
</tr>
<tr>
<td>374</td>
<td>0.417</td>
<td>7</td>
<td>3.33</td>
<td>93</td>
</tr>
<tr>
<td>392</td>
<td>0.071</td>
<td>7</td>
<td>3.17</td>
<td>43</td>
</tr>
<tr>
<td>429</td>
<td>1.3</td>
<td>1</td>
<td>3.7</td>
<td>55</td>
</tr>
<tr>
<td>452</td>
<td>0.098</td>
<td>11</td>
<td>3.58</td>
<td>36</td>
</tr>
<tr>
<td>519</td>
<td>0.035</td>
<td>7</td>
<td>2.4</td>
<td>28</td>
</tr>
<tr>
<td>Ti(^{1+}) ions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>0.6</td>
<td>6</td>
<td>4.96</td>
<td>45</td>
</tr>
<tr>
<td>336</td>
<td>1.6</td>
<td>4</td>
<td>4.9</td>
<td>103</td>
</tr>
<tr>
<td>346</td>
<td>0.062</td>
<td>10</td>
<td>3.71</td>
<td>53</td>
</tr>
</tbody>
</table>

Tab. 2.I. Data in the visible region for Ti target.

Finally, through a plot of \(\ln(I\lambda / Ag)\) against \(E\) for several spectra lines should be a straight line of slope \(-1/kT\) from that we can calculate the electronic temperature and with the relation (2.20) the electron density. The fig. (2.19) shows a calculation of this type [122] where the slope, relative to the Ti\(^{1}\) and Ti\(^{II}\) de-excitation lines, give an electron coronal temperature of 0.66 eV and an electron density greater of \(3 \times 10^{16} / \text{cm}^3\), in local thermal equilibrium conditions (LTE).
Fig. 2.19. Boltzmann plot of the optical spectroscopy analysis for Ti ablation at 270 mJ.

\[
\ln(\frac{I(\lambda)}{Ag}) \quad \text{vs.} \quad E_k \quad (\text{eV})
\]

- \(k_B T = 0.66\text{eV}\)
- \(n_e > 0.3 \times 10^{16}\text{cm}^{-3}\)
3 Laser applications to medicine

3.1 An introduction to physics of the laser-tissue interaction.

The interaction between the electromagnetic radiation and the biological tissue it is a phenomenon very complex since involves different physical aspects and different biological reactions. In fact, it is difficult to put together different basic concepts to describe nonlinear interactions such as tissue ablation and situations where the physical properties of tissue do not remain constant during laser radiation. A wide range of tissue reactions can be achieved by varying the laser pulse duration, energy per pulse, wavelength and spot size. In each case, the amount of energy absorber in a specific volume is critical.

In general, the transfer of the light energy into a tissue depends on three factors:
4. wavelength of the laser light;
5. power density of the laser;
6. chemical and physical properties of the target.

The absorption of the laser radiation by the tissue is given by the equation:

\[ I_t = I_o \cdot e^{-\alpha L} \]  

(3.1)

where \( I_t \) is the intensity of light transmitted, \( I_o \) the intensity of the light incident, \( L \) is the thickness of the tissue, and \( \alpha \) is the absorptivity of the target tissue. If the absorption is strong, the photons penetrate to a depth of only 0.1÷0.01 mm from tissue surface. The strong absorption tends to minimize the thermal damage to the underlying areas because the diffusion of heat from the laser photons is minimized. Also the lasers with shorter pulses minimize the lateral spread of heat or thermal damage.

The wavelengths of infrared photons correspond in energy to vibrational and rotational sublevels of excitation of the molecules of all biological tissues. This mode of energy transfer is known as “heat”, and is rapidly redistributed among the molecules and raises the temperature of target tissue. If the power density is some order of the kW/cm\(^2\) and the exposure time is some order of the milliseconds or longer, the temperature of the exposed region can rise above the boiling point of the water. Short-pulsed lasers with wavelength in the near-infrared such as Er:YAG, Ho:YAG and Er,Cr:YSGG can be well absorbed by the water component in tissue.

Fundamentally different are the absorption process of ultraviolet lasers from the absorption process of the visible and IR wavelengths. Absorption UV leads to excitation of the electrons that hold the atoms of the structural molecules together. This phenomenon, called electronic excitation, conveys the energy of the photon directly to the bonding electrons and facilitates the break up of these bonds. The process of
excitation itself can cause the bond break immediately or it can be happen subsequently. Table (3.I) shows an approximate calculation of the energy requirement for photons to excite the various energy levels present in molecules.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Photon Energy to Excite the levels (eV)</th>
<th>Approximate Spectral Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization band</td>
<td>≥ 6</td>
<td>Vacuum UV</td>
</tr>
<tr>
<td>Electronic</td>
<td>1,00</td>
<td>UV-A-B-C, visible</td>
</tr>
<tr>
<td>Vibrational</td>
<td>0,10</td>
<td>Infrared</td>
</tr>
<tr>
<td>Rotational</td>
<td>0,01</td>
<td>Microwave</td>
</tr>
</tbody>
</table>

Table 3.I. Absorption Region for Excitation of Biomolecules

In general, electrons can be excited into the ionization band by \( \lambda \) in the Vacuum UV (10 nm \( \div \) 190 nm). The remaining UV and visible regions can excite electrons from the ground state to various electronic excited states. Infrared radiation can excite molecules into higher vibrational states; microwave radiation excites molecular rotational energy levels.

The typical binding energy of an organic molecule goes from 3 to 4 eV, while the energy of a photon at 193 nm is 6.4 eV. This means that although electronic excitation is due to a specific excitation process at a given wavelength, the reactions that follow can not be equally specific. Heating effects as a result of UV excitation may occur, due either to a failure of the photons to break a bond and so heat the molecule, or because the bond energy is considerably less than the energy of the photon in this way the excess is available for heating [49].

The fig. (3.1) shows a schematic representation of the interaction of ultraviolet and infrared photons with tissue, respectively.
Fig. 3.1 Schematic comparison of the interaction of ultraviolet (a) and infrared (b) photons with tissue, respectively.

The mesh represents filaments of structural protein molecules interspersed with the water that constitutes the major part of tissue. If the photons are of ultraviolet wavelength, the energy is exclusively absorption by the proteins which are subjected to bond-breaking and following ablation. The water content is expelled mostly in a liquid state together to the pieces of protein and its gaseous products. If, instead, the photons are of infrared wavelengths, it is the water that absorbs most photon energy to produce steam. The resulting explosion tears the protein filaments apart.

As stated above, the laser-tissue interaction is a collective process in which a stream of photons interacts with a slab of tissue, where the stream of photons is expressed as power density and is one of two factors that control the density of excited molecules. This means that two, and even multi-photon excitations, become possible. Shortest is the time of the impulse, greater it is the probability that it will excite molecules by more than one photon. In fact, the ablative photodecomposition and photodisruption depends strongly on such multi-photon processes. The
same amount of energy, if delivered in a longer pulse results in simple single-photon reactions and heating effects.

In fig. (3.2), the process of photon energy transfer into target tissue is shown. This process can be separated into three individual steps:

4. absorption of the photon;
5. bond breaking;
6. ablation of the target tissue.

Fig. (3.2). Transfer of photon energy into target tissue.

In the top to the picture, the laser irradiation is absorbed through the mask. The mask is used for a precise radiation on the areas of the target tissue. In the middle, are shown the chemical bonds that are broken in the tissue by the photon energy. In the bottom we have the ablation products leaving the surface of the target at supersonic velocity and the etched or crater created. In some medical applications, the last step does not always follow because
the first two steps can already leave a transformed material useful to the purpose of the application [49].

The ablation of the tissue consists of an explosion in miniature as a result of extremely fast pressure increase, photodecomposition, and thermal effects. The ablative photodecomposition, typical of the UV photons, is not a thermal reaction. In contrast, the vaporization is a thermal process that occurs with non-UV laser reactions. In addition to the obvious thermal effects and vaporization, there are many non-thermal effects such as recoil, pressure wave formation, ionization, free radical formation, photochemical induced oxidation, multi-photon absorption process and mechanically induced shock waves [51, 52, 53]. When ablation does occur, there is a shock wave that travels in a direction exactly opposite to the direction of the expelled products: the shock wave travels into tissue [49]. Its presence has been detected and its passage timed by a piezo-electric pressure sensor that can be attached to an isolated piece of tissue [50]. The shock wave shows the time scale in which ablation occurs. If the photons are delivered to the tissue in a micro-second pulse, the shock wave also develops in a similar scale of time, demonstrating that the process of tissue break up is quite rapid [49]. Of particular interest it is the induced damage potential from shock to the artery wall. Shorter is the laser pulse, higher is the power density, and more violent is the force of ablation. Using laser intensities of the order of $10^{10}$ W/cm$^2$, the pressure of the shock wave is about 100 MPa.

### 3.2 Optical response of tissue to laser radiation

Generally, laser-tissue interactions can be divided in the optical response and in the resulting thermal or photochemical response. In this paragraph we will examine briefly the basic optical interactions. As the absorbed light
is converted in heat, one quantity of particular interest is the *rate of heat generation*, $S(x,y,z)$, defined as:

$$ S(x, y, z) = \mu_a(x, y, z) \cdot \phi(x, y, z) $$

(3.2)

where $\phi(x, y, z)$ is the *local fluence rate* [W/m$^2$] and $\mu_a(x, y, z)$ is the *local absorption coefficient* [m$^{-1}$]. When the tissue is irradiated with a laser beam, the fluence rate of the beam inside the tissue decreases exponentially according to Beer's law [49]. The attenuation, using a pulsed irradiation, is due to absorption and scattering of the collimated light according to the relation:

$$ H(z) = (1 - r_s)H_0e^{-\mu_t z} $$

(3.3)

where $H(z)$ is the energy per unit area of the attenuated laser beam [J/m$^2$], $H_0$ is the radiant exposure [J/m$^2$], $r_s$ is the Fresnel specular reflection (which is about 2% for light normal to air-tissue interface), and $\mu_t$ is the attenuation coefficient [m$^{-1}$] according to the relation:

$$ \mu_t = \mu_a + \mu_s $$

(3.4)

where $\mu_a$ is the *absorption coefficient*, and $\mu_s$ is the *scattering coefficient* with units [1/m], respectively. The relation (3.4) considers the processes of absorption and scattering as disjoint events. Concerning this, fig. (3.3.a) and fig. (3.3.b) show a three-dimensional simulation, written in MATLAB computer language, that represents the variation of the normalized fluence in function of $\mu_t$ and of the distance within the tissue, respectively. In order to simulate a wide range of tissue types, the absorption coefficient $\mu_a$ was varied from 0.0156 cm$^{-1}$ to 4 cm$^{-1}$ and the scattering coefficient $\mu_s$ was varied from 0.5 cm$^{-1}$ to 20 cm$^{-1}$.
Most tissue types have microscopic optical coefficients varying in the above mentioned ranges [123].

Fig. 3.3.a. Three-dimensional representations of fluence in functions of $\mu_t$ and of the distance within the tissue.

Fig. 3.3.b. Two-dimensional representation of the variation of the fluence with $\mu_t$ and depth within tissue.
Furthermore, laser-tissue interaction is viewed as the propagation of photons through a volume of randomly distributed absorption and scattering centres. Therefore the probability that a photon will be absorbed or scattered over a distance $\Delta z$ is given by:

$$P = \mu_t \Delta z$$

(3.5)

The fluence rate of scattering light at $\vec{r}$ is obtained by summing all of the light (radiance) through the point $\vec{r}$ according to the relation,

$$\phi_s(\vec{r}) = \int_{4\pi} L(\vec{r}, \vec{s}) \cdot d\omega$$

(3.6)

where $L(\vec{r}, \vec{s})$ is the radiance of scattering light [W/(m$^2$·sr)] and $d\omega$ the infinitesimal solid angle [sr]. The importance of the contribution of scattered light to the spatial distribution of the rate of heat generation depends not only on the absorption coefficient at location $\vec{r}$ but the relative ratio of the scattering coefficient to the attenuation coefficient. This ratio is called *albedo* according to the relation,

$$a = \frac{\mu_s}{\mu_a} = \frac{\mu_s}{\mu_a + \mu_s}$$

(3.7)

If $a$ is greater than about 0.8, then the diffusion approximation provides a reasonable estimate of the distribution of scattered photons. When the *albedo* is less than 0.6, photon scattered from the collimated beam tend to be absorbed within or near the beam path, especially for beam diameters larger than the penetration depth of the beam [49], $\delta$, where

$$\delta = \frac{1}{\mu_t} \quad [m]$$
Finally, another important parameter concerning the optical response is the reflection of the light. It can be described by considering a ray of light that incises with angle $\theta_1$, respect to the normal direction to the surface, upon a flat surface with index of reflection $n_1$. If the index of refractions of the two media are not matched, then the angle of reflection, $\theta_1$, and the angle of transmission, $\theta_2$, are bound by Snell’s law,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

and shown in fig. (3.4).

Fig. 3.4. Reflection and transmission of a non-polarized ray of light incident upon means with different indexes of refraction.

While, at a boundary, an estimate of the reflection of a ray of non-polarized light at angle $\theta_1$ can be done by using the Fresnel’s law,

$$r_f(\theta) = \frac{1}{2} \left[ \frac{\sin^2(\theta_1 - \theta_2)}{\sin^2(\theta_1 + \theta_2)} + \frac{\tan^2(\theta_1 - \theta_2)}{\tan^2(\theta_1 + \theta_2)} \right]$$

(3.10)
This relation is necessary for to calculate the reflected power per unit area for diffuse (isotropic) light incident between \( \theta_1 \) and \( \theta_1 + d\theta_1 \) on the interface of two layers:

\[
R = 2\pi r_f(\theta_1) L_0 \cos \theta_1 \sin \theta_1 d\theta_1
\]

(3.11)

where \( r_f(\theta_1) \) is the Fresnel reflection coefficient at \( \theta_1 \), and \( L_0 \) the radiance of scattered light when the diffuse is isotropic.

The specular reflection of diffuse light incident on an air-tissue interface, shown in figure 4, is given by

\[
r_{sd} = \int_{0}^{\pi/2} r_f(\theta_1) \sin(2\theta_1) d\theta_1
\]

(3.12)

When light travels from layer 2 (tissue) to layer 1 (air), all rays at an angle \( \theta_2 \) greater than a critical angle \( \theta_c \) are totally reflected. That is,

\[
r_f(\theta_2) = 1 \quad \text{for} \quad \theta_2 \geq \theta_c
\]

(3.13)

where the critical angle \( \theta_c \) is given by Snell’s law for \( \theta_1=90^\circ \) as

\[
\theta_c = \arcsin\left(\frac{n_1}{n_2}\right)
\]

(3.14)

The critical angle for total internal reflection in tissue at an air boundary is about 45° for \( n_{\text{tissue}} = 1.4 \) [65].
3.3 Thermal response

The thermal response of a biological tissue to laser radiation is governed by the local rate of heat generation as shown in eq. (3.2). In the absence of any phase change, an estimation of the transient temperature field is described by appropriate boundary conditions and from heat conduction equation [49]:

$$
\rho c \frac{\partial T(\vec{r},t)}{\partial t} = k \nabla T(\vec{r},t) + Q(\vec{r},t)
$$

(3.15)

where \( \rho \) is density [Kg/m\(^3\)], \( c \) is specific heat [J/Kg.°K], \( k \) the thermal conductivity [W/m °K] and \( Q \) is the rate of heat generation.

For an instantaneous point source in an infinite medium the transient temperature field, is given by

$$
T(\vec{r},t) = \frac{Q}{\rho c (2\sqrt{\pi}a)} e\left(\frac{-|\vec{r}|^2}{4a^2}\right)
$$

(3.16)

where \( Q \) is the amount of heat instantaneous generated a \( r = 0 \), and \( \alpha = k/\rho c \) is the thermal diffusivity [m\(^2\)/s].

For an approximate simulation, we will consider the one dimensional transient heat conduction equation:

$$
\frac{\partial T(z,t)}{\partial t} = \frac{k}{\rho c} \frac{\partial^2 T(z,t)}{\partial z^2} + \frac{Q(z,t)}{\rho c}
$$

(3.17)

where \( T(z,t) \) is the temporally and spatially varying temperature [°C]; \( Q(z, t) \) is the temporally and spatially varying laser power input, and \( z \) the depth from surface [135].

The heat generation term, \( Q(z, t) \) in eq. (3.17) is given by,
\[ Q(z,t) = (1 - r_s) F(t) \mu_a e^{(-\mu_a z)} \]  

(3.18)

where \( F(t) \) is the time dependent incident fluence of the laser pulse when the absorption is consistent with the Beer-Lambert law; \( r \) is the Fresnel reflectance and \( \mu_a \) is the absorption coefficient.

The meaning physical of the solution of the eq. (3.17) is the distribution of temperature given by [136]:

\[ T(z,t) = \frac{Q}{\rho c} \frac{1}{2\sqrt{\pi \alpha t}} e^{\left( \frac{z^2}{4\alpha t} \right)} \]

(3.19)

with the meaning of the parameters given above.

An approximate first calculation regard a simulation of the heat generation during argon laser irradiation (at 500 nm) on the surface of aorta when the incident fluence of the laser pulse is varying from 0 to 10 J/cm\(^2\) (Fig. (3.5.a)).

\[ \mu_a = 4 \text{ cm}^{-1} \]

Fig. 3.5.a. Predicted heat generation versus laser fluence in aorta.
The corresponding transient temperature field is shown in fig. (3.5.b) where the heat generation varies from 0 to 30 J/cm³ and the pulse duration from 0 to 1 second. The parameters used in this simulation were the thermal properties of human aorta: \(\mu_a = 4\ \text{cm}^{-1}\), \(\alpha = 1.27 \times 10^{-3}\ \text{cm}^2/\text{s}\), \(k = 4.78 \text{mW/cm} \cdot \text{°C}\) [55].

Fig. 3.5.b. Predicted transient temperature field versus heat generation and pulse duration.

Most of solutions of thermodynamic equations rely on computer simulations and approximate calculations. In some situations involving an air-tissue interface, the equation (3.15) not adequately describes the thermal process. This sources of errors can be of different nature:

- Optical or thermal governing equations do not represent the physical problem;
- The computer program does not correctly represent the governing equation;
- Values of the optical and thermal properties are not sufficiently accurate for required predictions;
- Possible sources of experimental errors into measures of parameters.
But excellent agreement between measured and computed temperatures have been reported for the eye [54]. Many possibilities of sources of errors can be found with a more careful analysis to the list above mentioned. In this direction, further simulations are in progress.

3.4 Application of laser in ophthalmology
The most medical application for laser technology in medicine has been in ophthalmology. The lasers mainly employed were the argon, krypton, argon pumped dye, Nd:YAG, and most recently diode lasers. Lasers have achieved remarkable clinical successes in the treatment of retinal diseases, glaucoma, and lens capsule opacification following cataract surgery.

The eye is one of the most accessible human organs, and its media (cornea, aqueous humour, lens, and vitreous) are transparent to visible light, allowing direct inspection of its internal structures for diagnosis and treatment. Many intraocular tissues contain pigments (such as melanin) that allow absorption of laser energy for photothermal laser-tissue interactions. Transparent intraocular structures (posterior lens, capsule and vitreous) have been also subjected to laser treatment with Nd:YAG photodisruptors.

Because this paragraph has the purpose to deal some applications of laser technology in ophthalmology, for a fuller treatment about ocular anatomy refers itself at specific medicine books. Here are briefly discussed the therapeutic applications of laser according to photothermal, photodisruptive, and photochemical mechanism of laser-tissue interaction.

Light entering the eye can be reflected, scattered, transmitted or absorbed. The principal parameter from to choose in ophthalmic laser surgery is a proper laser wavelength that is transmitted through the ocular layers to become incident upon the target tissue. In the visible and near infrared spectrum (400 nm to 1400 nm), the absorption characteristic of ocular tissue are determined by a group of chromophores within the tissue.
Ocular chromophores that absorb light in the visible spectrum include melanin, haemoglobin, and xanthophylls. The absorption spectra of these pigments are illustrated in fig. (3.6.a) together to the wavelength of four commonly utilized ophthalmic lasers: argon, krypton, dye and Nd:YAG [49].

Fig. 3.6.a. Transmission spectra of the major ocular chromophores: melanin (1), reduced hemoglobin (2), oxygenated hemoglobin (3), and macular xanthophylls (4).

Figs. [(3.6.b) and (3.6.c)] show the attenuation length vs. photon energy for water and polycarbonate (C_{16}H_{14}O_{3}) that represent the principal components in biological tissue. Synthetic polymers, are often used for to study the properties of the laser-tissue interaction [65].
Fig. 3.6.b. Attenuation length vs. photon energy for water.

Fig. 3.6.c. Attenuation length vs. photon energy for polycarbonate.

Fig. (3.7) shows, instead, as in the mid-infrared spectrum (1.8 µm ÷ 10.6 µm), the major molecules absorbing incident photons is water.
Fig. 3.7. Absorption spectra of water.

The retina contains at least six pigments: melanin, hemoglobin, macular xanthophylls, rhodopsin, cone photopigments, and lipofuscin. The first three are of major importance in laser photocoagulation of the retina. The cornea consist of five principal layers, the epithelium, Bowman’s layer, stroma, Descemet’s membrane and the endothelium as shown in fig. (3.8).
The cornea is protected continuously by a tear film that has a high lipid content and a high index of refraction \((n = 1.40)\). The cornea, due to transmission characteristics, provides an effective window for vision, photocoagulation, photodisruption, imaging and examination of intraocular structures.

### 3.4.1 Photothermal mechanism

The use of lasers as a selective heat source to coagulation retina tissue is one of the most important and widely adopted ophthalmic laser applications. It is a typical mechanism of photothermal laser-tissue interaction and occurs when laser energy is absorbed by the target tissue and is converted into heat.

The effects on the tissue depend from:

1. wavelength of the laser radiation;
2. absorption coefficient of the tissue;
3. power or energy density of the laser;
4. duration of laser radiation.

These parameters determine three predominant photothermal effects:

1. Photoheating;
2. Photocoagulation;
3. Photovaporization.

The photoheating happen for low (less than 10°C) temperature elevations that occur from many seconds to minutes and usually cause cell damage or death without causing structural alteration to the tissue. Greater temperature elevations (20-30 °C), occurring over shorter time intervals (≈1 sec.), and cause thermal coagulation of tissue, with cellular death and irreversible structural damage to the tissue due to denaturation (loss of the three-dimensional molecular structure) of tissue proteins (photocoagulation). Finally, the laser energy depositions that rapidly (<<1 sec.) heat the tissue above its boiling point cause thermally tissue removal by explosive vaporization (photovaporization).

To minimize the thermal damage of the surrounding ocular tissue during laser treatment, should be selected a wavelength that is preferentially absorbed by the target tissue with a laser exposure duration that should be shorter than the thermal relaxation time of the tissue, according to the relation

\[ T_h = \frac{d^2}{4k} \]

where \( d \) represents the absorption depth of the radiation, and \( k \) is the thermal diffusivity of the tissue.

For example, lasers operating into mid-infrared (2.94 µm) as Er:YAG and Er:YSGG, can be used for the cutting of the cornea because the water (k =
1.5\times 10^{-3} \, \text{cm}^2/\text{sec}) \, \text{at this wavelength (see Fig. (3.7)) is the primary absorbing molecule (d = 1 \, \mu m) with a thermal relaxation time calculated of 1.7 \, \mu s. Therefore, to achieve efficient photovaporization with minimum damage to the surrounding corneal tissue, the pulse duration of the laser must be significantly less than 1.7 \, \mu s. Shorter are the laser pulse duration, less are the thermal tissue damage as shown in the simulations of fig. (1.3.a) and fig. (1.3.b).

In Tables (3.II) and (3.III) \cite{49}, are summarized the present clinical and research applications for photothermal laser in ophthalmology, respectively.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Disease</th>
<th>Laser/Wavelength (nm)</th>
<th>Rationale</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan-retinal photocoagulation</td>
<td>Proliferative retinopathies</td>
<td>Argon-488/514</td>
<td>Destruction of peripheral retina decreases stimulus for new blood vessel growth</td>
<td>Widespread application</td>
</tr>
<tr>
<td>Focal macular photocoagulation</td>
<td>Diabetic macular edema, vein occlusions</td>
<td>Argon-488/514, Krypton 647, Dye-577</td>
<td>Focal treatment decreases leakage of fluid in retina</td>
<td>Widespread application</td>
</tr>
<tr>
<td>Photocoagulation of subretinal neovascular membranes</td>
<td>Age-related macular degeneration</td>
<td>Argon Green-514, Dye-577</td>
<td>Destruction of new vessel membranes prevents complication from subretinal hemorrhage and leaking vessels</td>
<td>Widespread application</td>
</tr>
<tr>
<td>Traeculoplasty</td>
<td>Open angle glaucoma</td>
<td>Argon-488/514</td>
<td>Focal photocoagulation of trabecular meshwork improves aqueous outflow, decreasing pressure</td>
<td>Compared favorably to medications in recent study Has replaced need for intraocular surgery</td>
</tr>
<tr>
<td>Peripheral iridotomy</td>
<td>Narrow angle glaucoma</td>
<td>Argon-488/514</td>
<td>Hole in iris allows alternative path for aqueous flow, preventing angle closure</td>
<td>Has replaced need for intraocular surgery</td>
</tr>
<tr>
<td>Cyclophotocoagulation</td>
<td>Advanced glaucoma</td>
<td>Nd:YAG-1064 free running thermal mode</td>
<td>Destruction of ciliary body decreases intraocular pressure</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.II. Photothermal laser applications in clinical use.
One of the most important application lasers as heat source is to coagulate retinal tissue. In the early 1960s, the energy from ruby laser (694 nm) was absorbed by the retinal pigment epithelium and caused photocoagulation of the outer retina. Improvement in the clinical setting have brought to using argon laser at 488 and 514.5 nm with irradiance of laser treatment of 100 W/cm² and an application time of 0.1÷1 second.

Another application of the photothermal mechanism is the laser corneal surgery. Although the healthy cornea is transparent to visible light and does not interact with argon (488/514 nm), krypton (647 nm) or dye (577 nm) photothermal lasers, wavelengths in the mid-infrared and infrared spectrum (1900 nm ÷ 10600 nm) are strongly absorbed, largely due to absorption of water, which composes ≈ 75 % of corneal tissue. As shown in fig. (3.9), the absorption increases sharply for wavelength longer than 2.5 µm until peak maximum near at 2.9 µm where the cornea’s IR absorption spectra is very like to the spectra of water.

Table 3.III. Photothermal laser applications in experimental development.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Disease</th>
<th>Laser/Wavelength (nm)</th>
<th>Rationale</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration surgery</td>
<td>Glaucoma</td>
<td>TmHoCr:YAG-2.1µm</td>
<td>Small incision, minimal trauma may increase survival of filtration bleb</td>
<td>Full thickness trephination possible in 7 s Early clinical studies</td>
</tr>
<tr>
<td>Corneal trephination</td>
<td>Corneal scarring and disease</td>
<td>HF 2.9 µm, Er:YAG-2.9 µm</td>
<td>Nonmechanical cutting may decrease postoperative astigmatism</td>
<td>Unsuccessful in clinical applications to date</td>
</tr>
<tr>
<td>Photothermal keratoplasty</td>
<td>Hyperopia</td>
<td>Ho:YAG</td>
<td>Shrinkage of collagen steepens central cornea</td>
<td>Unsuccessful in clinical applications to date</td>
</tr>
<tr>
<td>Laser tissue welding</td>
<td>Wound closure</td>
<td>Line-tuned HF 2.55 µm</td>
<td>Fusion of collagen and connective tissue</td>
<td>Unsuccessful in clinical applications to date</td>
</tr>
<tr>
<td>Cataract removal</td>
<td>Cataract</td>
<td>HF and other mid-IR 2.5-3.0 µm</td>
<td>Cataract removal while maintaining capsular bag</td>
<td>Will facilitate development of accommodating lens</td>
</tr>
<tr>
<td>Laser-induced hyperthermia</td>
<td>Ocular tumors</td>
<td>Mid-infrared</td>
<td>Selective heating causes tumor necrosis</td>
<td>Unsuccessful in clinical applications to date</td>
</tr>
</tbody>
</table>
Fig. 3.9. Light absorption coefficient vs. wavelength for the dehydrated, dehydrated human cornea and water. Within this spectral region, laser parameters such as wavelength, pulse duration, energy, density, can be chosen to cut, reduce, and weld tissue by photothermal mechanism.

Finally, another application of the photothermal mechanism is the laser tissue welding that involves the use of laser energy to fuse tissue directly or activate biological agents to bond tissue. It may allow the closure of the wound without suture and reduce so the surgical time and finds application in corneal, cataract, glaucoma, and vitreoretinal surgery. Probably this welding is due to tissue fusion caused to denaturation (loss of the three-dimensional molecular structure) and homogenization of collagen with interdigitation of individual fibrils (microscopic formation thin and lengthened, present in different tissues to form fibre) that occur when tissue is heated by absorption of laser radiation [124].

A disadvantage to laser applications utilizing photothermal mechanisms is that the laser wavelength and absorption properties of the tissue must be carefully matched. In fact, the tissues transparent to the incident wavelength will be not affected.
3.4.2 Photodisruptive mechanism

Nd:YAG laser operating at 1064 nm with short pulsed (≈ 30 ps for mode-locked and ≈ 10 ns for Q-switched) is used to create optical breakdown and photodisruption of ocular tissue. A sharp focus (≈ 10÷50 μm in diameter) through expander-focusing lens system it is employed to achieve extremely high irradiances (10⁸÷10¹¹ W/cm²) such that ionization of molecules occurs at the target. This ionization, in front the target tissue, brings to developed and creating plasma (collection of ions and electrons) that reached peak temperature ≥10⁴ °C. Shock waves emanating from the site of plasma formation cause mechanical disruption of structures adjacent to the site of optical breakdown. Because optical breakdown is a threshold phenomenon that depends on the strength of the electric field, photodisruption is not depend on absorption of the wavelength by the target tissue, and can be used in tissue that are transparent to the incident laser wavelength. In order that optical breakdown occurs, it is necessary for the photodisrupting laser delivery system to achieve the required high irradiance within a small volume of tissue. In table (3.IV) are summarizes the photodisruptors laser applications.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Disease</th>
<th>Laser/Wavelength</th>
<th>Rationale</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Posterior capsuleotomy</td>
<td>Capsular opacity after cataract surgery</td>
<td>Nd:YAG-106-1</td>
<td>Photodisruption allows small opening to be created without IOL damage</td>
<td>Widespread use — replaced need for intraocular procedure</td>
</tr>
<tr>
<td>Lysis of vitreous strands</td>
<td>After trauma, surgery</td>
<td>Nd:YAG-106-1</td>
<td>Adhesions can be severed without entering eye</td>
<td></td>
</tr>
<tr>
<td>Peripheral iridotomy</td>
<td>Refractive errors</td>
<td>Nd:YAG-106-1 2nd harmonic-562</td>
<td>Removing tissue from stroma changes corneal refractive power</td>
<td>Experimental</td>
</tr>
<tr>
<td>Endolaser vitreous surgery</td>
<td>Diabetes, trauma</td>
<td>Nd:YAG-106-1 Er:YAG-2.9 μm</td>
<td>non-contact cutting</td>
<td>Experimental</td>
</tr>
</tbody>
</table>

Table 3.IV. Clinical and research applications of photodisruptor lasers in ophthalmology.
The commonest and successful photodisruptor application is the creation of a posterior capsulotomy with a Nd:YAG laser carried out different years more late (following extracapsular cataract surgery) when the posterior capsule, left intact by the surgeon to support a plastic intraocular lens (IOL), opacifies due to proliferation of retained lens epithelial cells. The patient, who experienced improvement of vision following surgery, suffers slowly declining vision as the capsule opacifies. The surgeon uses the Nd:YAG photodisruptor to create a central opening in the capsule, restoring vision. The surgeon must be careful to focus on or slightly behind the posterior capsule, or undesirable pitting or cracking of the polymethylmethacrylate intraocular lens can occur [49].

3.4.3 Photochemical mechanism

In 1983 Trokel and Srinivasan noted, using a far-UV (193 nm) argon fluoride excimer laser, that corneal tissue could be removed discretely and precisely without any histological evidence of thermal damage to the adjacent corneal tissue recognized that the excimer laser could to offer a new approach to corneal surgery called corneal sculpting.

This photoablation occurs because the cornea has an extremely high absorption coefficient at 193 nm, and the photon at 193 nm are highly energetic (6.43 eV). This energy is greater of energy than the carbon-carbon bonds interlinking the protein molecules of the cornea. Consequently, the intermolecular bonds are broken and the discrete volume of corneal tissue is removed with each pulse of the laser as shown in fig. (3.10) [125, 126].
Fig. 3.10. 193 nm argon fluoride laser pulseds result in a unique photochemical interaction with the cornea termed photoablation. The laser pulse (a) is highly absorbed in the first several microns of corneal tissue, primarily by protein chromophores (b). Because the 193 nm photons have energy in excess of the carbon-carbon intermolecular bonds of corneal tissue, the bonds are photoelectrically decoupled, resulting in the ejection of many small fragments from the surface (c). The photoablation process is completed after 15 ns, leaving clean, precise edges with only 0.3 μm of adjacent tissue alteration.

The depth of the ablation depend on the radiation exposure and typically varies from 0.1 to 0.5 μm at a radiant exposure of 50 to 250 mJ/cm² as shown in fig. (3.11) [127].
Fig. 3.11. Ablation depth of the human cornea per pulse vs. radiant exposure with the 193 excimer laser. Tissue ablation rate will vary with the hydration of the cornea.

Between other excimer lasers operating in far-UV at 157, 248, 308 and 351 nm that have been investigated, the 193 nm wavelength generated by the argon fluoride excimer laser has achieved the best quality for corneal excisions.

A application particularly important of the excimer laser is its ability to sculpt or reshape the outer surface of the cornea to correct refractive errors. This relatively new surgical procedure was named PhotoRefractive Keratectomy (PRK) by its developers (Fig. 3.12) [128].
Fig. 3.12. Photorefractive keratectomy (PRK) for myopia with the 193 nm excimer laser. The stromal surface of the cornea is ablated with the laser following removal of the epithelium by the surgeon (a). Following re-epithelialization, the anterior corneal curvature is flatter, reducing myopia (b). Preliminary evidence indicates that this technique is safe and effective for reducing myopia up to 6 diopters.

Present data indicate that PRK appears to be a safe and effective method for reducing myopia up to 6 diopters with few side effects or complication [129-132]. Treatment of myopia greater than six dioptres has been less successful due to regression of the refractive effect caused by corneal
wound healing [133]. This treatment surgical laser may offer an alternative to glasses and contact lenses for millions of myopic individuals, and may represent the most widespread medical application for a laser [134]. In this direction, further studies are in progress.

3.5 An application of pulsed laser in medical dentistry

Pulsed laser were introduced to dental research in the early 1960s and are now used in several specific areas of application, such as surgical treatment of oral malignancies and periodontal diseases, dental caries detection and control, and preparation and sterilization of root dental canals [56]. In spite of these advances, laser are still limited in their ability to remove sound tooth structure since elevating the temperature in the tooth can generate adverse effects at the surface and in tooth pulp. Ablation efficiency, thermal damage, and final surface characteristics are the ultimate test to any laser effectiveness.

In the past few years, several infrared lasers have been proposed for hard tissue applications. In particular Er,Cr:YSGG pulsed laser has been proposed as candidate for efficient hard tissue ablation since its high absorption coefficient allows an large energy/volume deposition and minimal heat diffusion, which improves ablation rates with minimal collateral thermal damage [57].

The erbium, chromium: yttrium, scandium, gallium, garnet (Er,Cr:YSGG) laser, in fact, operating in the infra-red spectrum at 2780 nm shows a strong peak in the absorption spectrum of hydroxyapatite and water which leads to a high efficient ablation [58]. In fig. (3.13) we have a comparison of the absorption coefficients for water, hydroxyapatite (HA) and dentine vs. wavelength. At 2.78 µm the absorption coefficient is about $10^4$ cm$^{-1}$ and 350 cm$^{-1}$ for H$_2$O and dentine, respectively [63].
Fig. 3.13. Absorption coefficient of the water, dentine and hydroxyapatite vs. wavelength.

The hydroxyapatite (HA) has the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ chemical composition and is contained in the concentration of 97% in the dental enamel. The water content of enamel is about 2.5% and that of dentine 13%. These materials weakly absorb the radiation in the visible and near-IR spectral region \[64\]. Laser irradiation, in particular, causes thermally induced changes on the enamel and dentine surfaces. It produces surface roughness and irregularities, similar to that of an acid etching, to a depth of the order of 10 to 20 $\mu$m, depending on the type of laser, amount of applied pulse energy and photon energy. The etching occurs through a process of continuous vaporization and micro explosion, resulting from vaporization of water trapped in the hydroxyapatite matrix \[59\]. The laser infrared irradiation of dental hard tissues modifies the calcium-to-phosphorus ratio, reduces the carbonate-to-phosphate ratio and water and organic
components contents, and leads to the formation of more stable and less acid-soluble compounds, thus reducing susceptibility to acid attack and caries, and suggesting that laser etching might create re-mineralization micro spaces that trap free ions [60, 61, 62]. Erbium laser offers the ability to remove enamel, dentine and carious with minimal amounts of thermal disruption to the residual tooth. Thus, laser-induced caries resistance would be of great importance in dentistry.

In this investigation the Er,Cr:YSGG pulsed laser, operates at a wavelength of 2.78 µm with a pulse duration of 140 µs and a repetition rate of 20 Hz. The maximum energy pulse is variable from zero up to 300 mJ. The laser energy is delivered through a fiber optic system to a sapphire tip that has a terminal diameter of 600 µm and is bathed in an adjustable air/water spray. Thus, the laser energy is strongly absorbed by the water micro droplets, which are partially responsible for the hard tissue cutting effects, as reported in literature and designated as hydrokinetic system (HKS) technique and schematized in fig. (3.14) [59].

Fig. 3.14. Schematic hydrokinetic (HKS) system technique.
In this experiment, the energy pulse output was set from 25 mJ up to at 275 mJ, yielding an energy surface density (fluence) from 8.8 J/cm$^2$ to 97.2 J/cm$^2$, respectively. The measurements of ablation yield vs. the laser fluence for dry dentine are reported in figure 15 for low laser fluence, in order to identify the ablation threshold below which no ablation occurs [63].

![Graph](image)

**Fig. 3.15.** Dentine ablation yield vs. laser fluence and profile of the crater (inset).

The interaction of the laser light with the dentine target produces a crater whose profile is shown in inset of fig. (3.15). This crater profile have been investigated at low laser fluence, irradiating the dentine target with 100 mJ laser energy, an irradiation time of 10 s and a repetition rate of 20 Hz. This procedure permits to evaluate the ablation yield in terms of removed mass per pulse. At higher laser fluence the removed mass can be measured by the dental weight difference between the before and just the laser ablation. The fig. (3.16) shows a SEM micrograph of a typical ablation crater of dentine [63].
Fig. 3.16. Photo of the typical ablation crater in dentine target at 275 mJ laser energy, 10 s irradiation time and 20 Hz repetition rate. Of particular interest (fig. (3.17)) are the compares between the ablation threshold in dentine with IR laser with the ablation thresholds of HA obtained with visible and UV lasers, respectively.

Fig. 3.17. Comparison between the dentine ablation yields obtained with IR (2780 nm) laser with that of HA ablated with UV (308 nm) and VIS (532 nm) lasers.
The trend shown in figure indicate that the ablation yield grows linearly with the laser fluence and that the Er,Cr:YSGG laser induces higher ablation effects with respect to other lasers, as result of the high absorption coefficient and the use of the air-water integrated spray to the handpiece. In fig. (3.18) we have a picture of such handpiece.

![Handpiece](image)

**Fig. 3.18. Photo of the handpiece relating to the Er,Cr:YSGG laser.**

For a greater investigation in the laser irradiation on dentine target, the fig. (3.19) compares the ablation yields of dentine obtained fixing the water percentage of the spray system and changing the air percentage at three different values of the laser pulse energy [63].
Fig. 3.19. Comparison of the ablation yields of dentine obtained fixing the water percentage of the spray system at 95% (a), 80% (b), 60% (c) and changing the air percentage for three different values of the laser pulse energy.

At high water spray percentage the ablation growth with the air content, as in fig. (3.19.a) and fig. (3.19.b) while at low water content (60%) the ablation shows a maximum at about 40% air, as reported in fig. (3.19.c).
Generally the high ablation efficiency is obtained with high percentage of water and about the same percentage quantity of air. This thesis is confirmed by other experiments obtained fixing the air percentage and varying the water content of the spray system, as shown in fig. (3.20) [63].

![Graphs showing ablation yields with different water and air concentrations](image)

**Fig. 3.20.** Comparison of the ablation yields of dentine obtained fixing the air percentage at 20% (a), 40% (b), 60% (c), 80% (d) and varying the water content of the spray system for three different values of the laser pulse energy.

The ablation yield decreases if the two concentrations of water and air are different, while increases when these two concentrations are similar. The higher values can be obtained for water/air ratio of about 95% / 80% and high laser fluence.

In fig. (3.21), we have a comparison of the ablation yield and crater depth versus laser energy for different air/water ratio.
This figure shown that above a laser pulse energy of 100 mJ (corresponding to a fluence of 33.3 J/cm²) the ablation yield saturates. Probably, this is a result of the high absorption of the ablation vapor and of the air/water mixture [63].

These results confirm the validity of the HKS technique. Hydrokinetic tissue-cutting refers to the process to removing hard biological material through the use of high speed controlled water droplets. Strong absorption of laser energy by fine water droplets results in a violent yet controlled micro expansion inducing strong mechanical forces on targeted tissue surfaces. Resulting hydrokinetics forces produce mechanical separation of the calcified tissue surface, yielding quick and clean tissue removal. Other factors at the tissue interface that involve water, mineralized tissue, and photon energy may also contribute to the cutting effect.
The laser wavelength, pulse width, wavelength-dependent absorption and energy density are critical in determining the relative amount of ablated material. Also the water-air spray system determines the value of the ablation yield, permitting to ablate dental tissue in normal environment and contemporary to remove irradiated mass from the deep crater. Increasing the laser fluence and the water and air flux spray the ablation yield increases.

Infrared radiation at 2.78 µm, obtained by the fast pulsed Er,Cr:YSGG laser can be employed very well to ablate dental tissues because of its high photon absorption. The strong absorption tends to minimize the thermal damage to the underlying areas because the diffusion of heat from the laser photons is minimized [65]. The air/water integrated atomizer spray helps the removal of the tissues without collateral thermal damage. The deposited energy from the IR photons is achieved through direct tissue absorption (linear or nonlinear). In these conditions, material can be removed by such processes as vaporization, melt removal, and burning. This radiation can break chemical bonds and induce chemical reactions, generating ablation with low thermal contributions. Moreover, the application of the water, to the investigated energy, should not damage the pulpal vitality of the tooth.

Finally, in fig. (3.22) the ablation rate of our data are comparable with the literature for middle energy of 40 mJ/pulse and repetition rate of 10 Hz respectively.
Fig. 3.22. Comparison the ablation rate of our data with the literature.

Er,Cr:YSGG laser ablation rate, over the range of energies tested, is not much higher than that of the Ho:YSGG or Er:YSGG used in similar experiments [66, 67]. Probably, it appears that for normal mode system an efficient ablation at a given parameter set (pulse duration, pulse energy, spot size, etc.) does not proceed until plasma is initiated. Once plasma is initiated, an efficient coupling of energy is possible in order to obtain the best control of the ablation yield efficiency and to operate correctly from the point of view of the medical aspect [63].
4 Laser application in biocompatible materials

4.1 Introduction to the biocompatible materials

A biomaterial is a conceived material as interface with the biologic systems to evaluate, to give support or to replace an any tissue, organ or function of the body (II International Consensus Conference on Biomaterials, Chester, Great Britain, 1991). Of particular interest it is the definition of biocompatibility: the biocompatibility of a material consists into characteristic of establishing favourable interactions with the living systems which it comes in contact. The biocompatibility is a fundamental requisite, bound by the necessity to improve and/or to repair a defined biologic function, without interfering or interacting into harmful way with the physiologic activities of the organism. For this reason one must hold an account of the degree of compatibility that depends on the form, structure, chemical composition and properties chemical, physical, mechanical and electrical, respectively. Furthermore, the degree of compatibility depends from site of location in the organism and from the type of application.
The interaction of biomaterials with the organism is a process at two ways because any installed material causes a reaction in the organism and to the same time suffers the attack from the organism. This means that exists a response of the organism to the implant of biomaterial and therefore no material is quite inert into biologic environment.

The response of the organism depends on the nature, characteristic and localization of the material and from the physiologic state of the receiver. While the phenomena of the integration among tissue and engaged material are closely correlated to the superficial properties of the implant. In fig. (4.1) we have a classification of the biomaterial.

<table>
<thead>
<tr>
<th>In base to produced effects on the materials</th>
<th>In base to interaction material/organism</th>
<th>In base to chemical nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Bio-stable</td>
<td>• Bio-toxic</td>
<td>• Polymeric</td>
</tr>
<tr>
<td>• Bio-degradable</td>
<td>• Bio-active</td>
<td>• Metal</td>
</tr>
<tr>
<td></td>
<td>• Bio-inert</td>
<td>• Ceramic</td>
</tr>
<tr>
<td></td>
<td>• Bio-reabsorbed</td>
<td>• Composite</td>
</tr>
</tbody>
</table>

Fig. 4.1. Biomaterials classification.

In the first box, the biomaterials are classified according to effects that produced on material: they are called **bio-stable** if don’t suffer substantial chemical transformations and physical in the time; **bio-degradable** if suffer substantial chemical transformations and physical that it brings them disappearing in the time.

In the second box, the biomaterials are classified according to the interactions material/organism. The **bio-toxic** are materials that provoke a rejection of reaction from biologic tissue because of processes of chemical type and/or galvanic. Belong to these classes some alloys to nickel base, cadmium, vanadium, some carbon steels, carbides and methyl methacrylate and other toxic elements.
The **bio-active** materials they favour biochemical interactions directly with the biologic tissue. The biologic tissue can grows on the surface of the material and allows establishment of a mechanical solid bond among natural tissue and prosthetic implant. Typical examples of bioactive materials are ceramic materials, such as hydroxyapatite and bio-glasses.

The **bio-inert** materials are stable from the point of view chemical and physical. They present minimum interactions with surrounding tissue and permit a good coexistence among organism and implant. Belong to these classes the tantalum oxides, titanium, aluminium, zirconium and UHMWPE polyethylene.

Finally, we have the **bio-reabsorbable** materials that suffer a progressive degradation into biologic system without to cause rejection reactions or toxic effects. Typical examples of absorbable materials are calcium phosphates, hydroxyapatite porous and some bio-glasses.

In the third box, the biomaterials are classified according to chemical nature. First we have **polymers**, constituted by molecules of elevated molecular weight. These molecules, called **macro-molecules**, are generally organic and they originate themselves from the concatenation of a large number of small unities, called **monomer**, which forms long chains of linear, branched and reticulated form, respectively. In fig. (4.2) we have three examples of these polymers.
For their intrinsic properties and resemblance with the natural polymers, they find a vast applications field as biomaterial.

Subsequently, we have the metallic biomaterials characterized from the metal bond where every atom it puts at disposal of all the crystal his valence electrons that form a cloud electronic mobile and generate a bond not-directional that is responsible of some peculiar characteristics of the metals (e.g. electric conductivity and thermal).

Then we have the ceramic materials. They are compounds inorganic refractory and contain metal elements and not metal. Since does not exist an univocal definition of ceramic materials, we can only say that they are classifiable neither as metals nor as polymers. They can present oneself as solids polycrystalline, amorphous or mono-crystalline. The bond primary present is a mixed ionic -covalent, where the ionic percentage of the bond influences on the crystalline structure of the material. Generally, they are compound of the type $A_mX_n$ where $A$ is the metal element and $X$ not metal element; $m$ and $n$ are integer.
Finally, we have the composite materials. These materials contain two or more components or constituent phases, whose characteristic properties are very different respect to that one of a homogeneous material. Since these characteristics can be changed, they find important applications technical and industrial.

4.2 Biocompatible film deposition by using pulsed laser

The innovative use of biomaterials to repair and reconstruct diseased or damage parts of the body has improved the quality and the length of the life for thousands of people. Several biomaterial compositions have been tested, but few have achieved human clinical application [68, 69, 70]. Clinical success requires the simultaneous achievement of a stable interface with tissue and a match of the mechanical behaviour of the implant with the tissue to be replaced [71]. In particular, calcium-phosphorous compounds have a fundamental role because of their attitude to induce bone-integration and to anchor rigidly prostheses or implants to the bone [76]. Between many calcium-phosphorous compounds, hydroxyapatite (HA) is the most important because it, especially if in crystalline form, shows a low solubility in the biological environment. It is contained at high concentration (~ 70%) in the cortical bone and in the dental enamel (~ 97%); for this reason it is recognized as an excellent biomaterial. Hydroxyapatite has Ca_{10}(PO_4)_6(OH)_2 chemical composition, crystallizes in an hexagonal phase, lattice group P6_3/m. Its unit cell contains six (PO_4)^{3-} tetrahedral groups. The density is 3.1 g/cm^3, the Young modulus 100 GPa and the thermal expansion coefficient 10^{-5} °C^{-1}, very similar to that of many titanium alloys.

The most interesting substrate, in dental and orthopedic field, that may be coated with HA are Ti and its alloys, such as Ti_6Al_4 and TiAl_6V_4, and hydrogenated polymers, such as polyethylene (PE) and
polymethylmethacrylate (PMMA). These implants coated with HA offer high mechanical integrity of a metallic device and high biocompatibility with the natural mineral composition of the bone. Carbon, titanium and polyethylene coatings improve the biocompatibility of the surface and modify significantly the chemical and physical properties of the covered surface. Carbon, for example, is hemocompatible and can be used for surfaces which are in contact with the blood, such as artificial blood vessels. Titanium oxide is inert and it can be employed for chemical passivation different surfaces, such as those in stainless steels. Polyethylene is a hard polymer which can be used so as a shock-absorber of stresses or so as a repellent water surface [77]. Deposition techniques at high temperature decompose HA and polymers. In vacuum, at about 850 °C HA dehydrates producing calcium oxides, tri-calcium phosphates and other Ca-P compounds, which have an high rate of re-adsorption [78] and polymers have a low melting points, generally below 200 °C.

Pulsed laser deposition (PLD) permits to deposite metal, ceramic and polymer coatings in vacuum preserving their original properties. In this work the application of Pulsed Laser Deposition (PLD) technique to HA and to other biomaterials will be presented and discussed using a Nd:YAG pulsed laser operating at fundamental (1064 nm), second harmonic (532 nm) and third harmonics (355 nm). It works with short pulses of 3-9 ns duration with a repetition rate from 1 to 30 Hz, a pulse energy from 3 mJ up to 300 mJ and laser fluence ranging between 0.3 J/cm² and 30 J/cm². As shown in experimental set-up of fig. (4.3), the laser beam was focused with a convergent lens through a thin glass window on the target, which was disposed in a vacuum chamber at 10⁻⁶ mbar. The laser spot was smaller than 1 mm² while the incidence angle was 45° [77].
HA and PE targets, consisting of pressed pellets, were obtained from powder sintered at relatively high temperature and pressure. C and Ti targets were used as pure metals supplied by Goodfellow. Generally substrates were silicon and titanium and the target-substrate distance was 65 mm. The particle emission occurs mainly along the normal to the irradiated target surface.

Laser light interaction with the target surface causes a very fast energy deposition in a thin surface layer with a consequent emission of vapor containing neutral, cluster and ion species. The energy of the particles ejected from the laser-generated plasma reach kinetic energy of the order of keV and their deposition produces ion implantation with a consequent high adhesion of the film to the substrate surface [79].

A first analysis regards the study of the craters on the target. Fig. (4.4.a) shows a photo of a typical ablation crater of Ti and its depth profile obtained irradiating the Ti target with 100 mJ laser energy, 60 sec irradiation time at 30 Hz repetition rate. The Ti crater depth is 1.6 mm and
the crater diameter is 1 mm. By measuring the crater volume and by using the Ti density, the removed mass from the crater was 1.0 µg/pulse, corresponding to an ablation yield of 1.2x10^{16} atoms/pulse [80].

Fig. 4.4. Photo of a typical ablation crater in Ti and its profile (a) and of HA crater and its profile(b) at 100 mJ laser energy, 60 s irradiation time at 30 Hz repetition rate.

In the same experimental conditions, i.e. by using a laser fluence of 10 J/cm^2 at 30 Hz repetition rate for 1 minute of irradiation, the photo of the HA crater and the crater shape are shown in fig. (4.4.b). The HA crater depth is 2 mm and the crater diameter is 1 mm. By measuring the crater volume and by using the HA density, the removed mass from the crater was 0.91 µg/pulse, corresponding to an ablation yield of 5.4x10^{14} molecules/pulse [80]. For C-target, at the maximum used fluence of 5.7 J/cm^2, the ablation yield was 4.5x10^{17} C-atoms/pulse [83]. The etching yields for Ti, HA and C increase with the laser fluence for different wavelengths and pulse duration, as reported in fig. (4.5) [77].
Fig. 4.5. Ablation yield vs. laser fluence.

At low laser fluence a threshold occurs, below which there is not ablation. The experimental fluence thresholds is about 0.55 J/cm², 2.4 J/cm² and 0.90 J/cm² for Ti, HA, and C respectively, in agreement with the literature data [81, 82].

In fig. (4.6) is reported the experimental HA etching yields comparison with the literature data relative to other laser wavelength as a function of the laser fluence. The ablation rates show an energy threshold depending on the depth penetration of the employed light in HA, which means on the minimum amount of energy need to evaporate the irradiated mass [80, 84].
At 248 nm (KrF excimer laser) the absorption coefficient is high ($3.6 \times 10^3 \text{ cm}^{-1}$) and the irradiated mass is low, thus the threshold is lower. On the contrary, at 694 nm (ruby laser) the absorption coefficient is low ($1 \times 10^3 \text{ cm}^{-1}$) and the irradiated mass high, thus the threshold is higher. Above the threshold, KrF laser produces a high density of HA plasma in front of the target surface, which absorbs part of the energy of the same impinging laser pulse and ablation yield saturation is reached suddenly. The lower density of the plasma produced by the XeCl laser produces a saturation effect at higher laser fluence with a consequent increase of the resulting ablation yield. The lower density of the plasma produced by the ruby laser (694 nm) and the Nd:YAG laser (532 nm) is very low; it does not absorb sufficient pulse energy, and a linear relation between the ablation yield and the fluence occurs [80].

Measurements demonstrate that the plume of the ejected material from the target is direct normally to the target surface, independently of the incidence angle of the laser. Fig. (4.7) shows a CCD image of the plasma,
performed with a camera triggered with the laser pulsed at 5.7 J/cm², taken with an exposition time of 1 µs. The visible plasma emission shows a very intense white light, with an ellipsoid shape, oriented along the normal to the target surface characterized by a mean volume of about 700 mm³ [83].

Fig. 4.7. CCD image of the plasma performed with a high resolution CCD camera.

This image permits us, as a first approximation, to estimate the plasma density by considering the visible volume of the plasma plume and the number of atoms/pulse ejected from the crater. In fact, with an ablation yield value of 4.7x10¹⁷ atoms/pulse and a mean volume of about 0.7 cm³, the atomic plasma density is:

\[
    n \approx \frac{4.7 \cdot 10^{17} \text{ atoms}}{0.7 \text{ cm}^3} \cong 6.7 \cdot 10^{17} \text{ atoms/cm}^3
\]  

(4.1)

Further, because the ion emission is about 70% with respect to the neutral emission and assuming the mean charge state to be \( < z > = 2 \), the electronic density of the plasma is \( n_e \cong 9.4 \cdot 10^{17} / \text{cm}^3 \).
The angular distribution of the ejected material from the irradiated HA target generally is of about 60° (FWHM), as reported in literature [85].

The laser light interaction with HA target causes a fast emission of vapor, clusters and micro-grains, which can be deposited on the near substrate as a thin film. Generally PLD films are not uniform in thickness, as measured by RBS analysis, and present different morphologies depending on the deposition angle, as observed by SEM photos of HA PLD film in the thick and thin region, respectively [86]. Two distinct regions in the angular distribution of deposited molecules are present. The first is a thicker film region in the central zone, orthogonal to the target-laser impact, and the second is a thinner region located at large emission angles.

For the HA deposition, the first region is granular, with 3-4 µm average size, while the second region shows a molecular deposition with grain size below 2 µm.

![SEM images of the film deposited along the normal to the target surface (a) and at large angles (b), histogram of the grain size distribution (c) and EDX analysis (d).](image-url)
The SEM micrographs of fig. (4.8) show the HA film deposited on Si along the normal to the target direction (a) and of the film deposited at angles higher than 40° (b), the histogram of the grain size distribution (c) and the EDX analysis giving the stoichiometric composition of the deposited film (d) [77]. EDX and RBS analysis show that the Ca/P ratio in PLD and PSD films is 1.75, in good agreement with the expected value measured in the initial target. However, this value indicates that about 3 mol % P$_2$O$_5$ can be loss and this causes an excess of about 5 mol % of CaO.

XRD analysis was used to identify the HA crystallinity and the phase of the deposits, as reported in the spectra of fig. (4.9) indicating a typical spectrum obtainable at large angles, $\phi = 30^\circ$, and low angles, $\phi = 0^\circ$, with respect to the target-normal direction [77].
Fig. 4.9. XRD comparison of PLD films deposited at different substrate angles.

The grain size distribution is large (fig. (4.10.a)) and it doesn’t depend on the grain sizes of the irradiated target but only by the kind of employed PLD system, i.e. laser wavelength, substrate temperature and substrate surface.

Laser wavelength, pulse width and energy density are critical in determining the relative amount of material deposited both such as granular components and molecular component. The grain size generally increases with the laser wavelength, as reported in fig. (4.10.b), in agreement with literature. However our measurements reported in fig. (4.10.a), indicate a high average grain size with respect to literature data [87]. The HA films
deposited both on Ti and Si substrates have an average grain size of about 15 µm, a factor 5 higher with respect to those obtained in similar conditions by using the ruby laser [80]. This is a very important result because in this field of research the best method of HA deposition should...
give high granular films and porous films in order to optimize the surface reactivity with the bone tissue increasing the anchorage of the bio-ceramic film with the biological tissue.

The Raman spectroscopy was employed to characterize the quality of deposited films. Literature reports that XRD (X-Ray Diffractometry) analysis identifies the crystallinity and the phase of the deposits. PLD films deposited at room temperature are amorphous, whereas those deposited above 350 °C are polycrystalline. In particular the photo-deposition at temperatures above 800 °C produces diffraction peaks typical of tricalcium-phosphate (TCP) [88].

The activity of the OH$^{-}$ group in the HA lattice is not sufficient to establish the difference between HA and TCP, while that of PO$_4^{3-}$ ions does it. Tetrahedral PO$_4^{3-}$ free ions present four normal modes of vibration, all of these vibrations are Raman actives, only $\nu_3$ and $\nu_4$ are infrared active. They were found to be $\nu_1 = 938$ cm$^{-1}$, $\nu_2 = 420$ cm$^{-1}$, $\nu_3 = 1017$ cm$^{-1}$, $\nu_4 = 567$ cm$^{-1}$ by means of Raman scattering measurement on phosphate in aqueous solutions [89].

These frequencies correspond, respectively, to the asymmetric P-O stretching mode, the doubly degenerate O-P-O bending mode, the triply degenerate asymmetric P-O stretching modes and the triply degenerate modes of mainly O-P-O bending character. In apatite crystals, all the modes are splitted into two or three bands and shifted because of the site symmetry and correlation effects due to the dynamic interaction between ions. The Raman spectra show well defined bands and a strong peak at 966 cm$^{-1}$, as reported in fig. (4.11) [80]. The comparison with standard sample demonstrates that the strong peak is due to a (PO$_4$)$^{3-}$ group bonded to HA while the shifted peaks, near 950 and 970 cm$^{-1}$, are typical of the groups bonded to TCP [90].
The comparison between the Raman spectra in HA target and in PLD HA film, obtained at 400 °C substrate temperature, as measured by a thermocouple stuck on the back-face of the substrate placed at 10 cm distance from the target, indicates a good reproducibility of the deposited film with respect to the target.

Fig. 4.11. Raman spectroscopy comparison for Target and thin films deposited at room temperature and at 400 °C.

But the HA deposition far from the target, at distances of about 30 cm, at which the thermocouple gives a temperature below 70 °C, indicates a differential structure of the film that is typical of an amorphous phase. In our experiment the temperature of the substrate is produced by the hot plasma laser generated in front of the substrate during the ablation with 30
Hz laser repetition and the Raman spectroscopy is performed in films deposited for times of 20 minutes [80]. This result is in agreement with the literature data and confirms that the HA structure growth is a thermal assisted phenomenon [88].

As said previously, PLD produces high energetic particles ejected from the laser-generated plasma plume whose energy, along the normal to the target surface direction, reaches values of the order of keV [79]. These particles are implanted in the first layers of the exposed surface producing high film-substrate adhesion. As an example, fig. (4.12) reports the result of energy measurements of aluminium neutrals and ions produced by 532 nm laser and 170 mJ energy, emitted at 0° angle with respect to the normal direction, whose energy has Boltzmann distributions, with mean values of the order of hundreds eV, and increases with the charge state [77].

Fig. 4.12. Particle energy distribution of aluminum plasma ablated at 170 mJ.

The adhesion of HA coatings to Ti or Ti alloy substrates has been evaluated using scratch tests and AES analysis. The scratch tests demonstrate that the HA films are very adherent to the titanium substrate, especially if the
substrate is heated at 400 °C. This effect can be explained on the base of the ion implantation of energetic Ca, O and P ions in the Ti surface and in the thermal diffusion of these species at 400 °C temperature, as demonstrated by the Auger depth profiles in the substrate reported in fig. (4.13) [77].

![Graph](image)

**Fig. 4.13. AES depth profile of HA diffused and implanted in Ti substrate at 400° C.**

In conclusion, we can say that PLD technique shows some advantages and potentiality to deposit thin biomaterial films on different substrates: production of high film uniformity, production of large grain deposition, fast deposition method, deposition in vacuum or in gas controlled environment, as obtained in our investigations. Moreover, literature reports that PLD produces polycrystalline HA coating, that show a high degree of phase purity; low non-stoichiometric component; good film-substrate adhesion (at relatively high substrate temperature); possibility to depose
films on polymers and various Ca-P compounds in presence of reactive gases.

Laser wavelength, pulse width, energy density, angles of deposition (with respect to the target-normal direction) and substrate temperature are critical in determining the relative amount of ablated material, deposited thin film and the morphology of the deposited film.

Increasing the laser fluence increases the ablation yield, the velocity of the film growth, on the substrate, and the adhesion of the film to the substrate surface. Decreasing the laser wavelength the deposited species have lower molecular weight and lower grain size, as demonstrated. Infrared radiation can be employed very well to ablate metallic target because of the high photon absorption from free electrons of the target that induces thermal processes and high vapour pressure. On the contrary, high gap insulators (polymers and ceramics) absorb very well UV radiation that breaks chemical bonds and induce chemical reactions, generating ablation without thermal processes. Visible radiation has an intermediate role and, due to its significant absorption in different materials, can be employed very well in PLD. The ablation threshold decreases using UV photons and increases with infrared photons [92]. Because high film porosity is important for HA, but not for Ti films, the ablation conditions can be chosen accurately in the two cases. A low laser fluence needs for titanium, in order to avoid emission of clusters, and a high fluence needs for HA, in order to promote large clusters emission.

The correct HA stoichiometry on the substrate, despite the fact that HA spontaneously decomposes in Ca$_3$(PO$_4$)$_2$ and CaO at about 900° C [93], is explainable on base of the very short time scale of heating process with can prevent decomposition prior to the phase transition from solid to melting state and/or vapour happens [86].
The angle of deposition is, probably, bound to the angular distribution of the material ejected with a $\cos \theta$ law. This law is explained on base of a simple evaporation process from a point source in according to Maxwellian velocity distribution of thermal emitted particles, as discussed in chapter 2.

Micron-sized particles photo emission may be explained by different theoretical mechanism induced in the irradiated target, such as laser ablation and shock wave generation. In the first case the strong molecular emission may be ascribed to high density of molecular bonds breaking and formation of ionized molecular gas. In the second case the process may be recognized as due to generation of shock waves. The absorption of short laser pulses at a target surface, in fact, can produce large pressure waves travelling into the material. When the compressive stress reaches a free surface of the irradiated material, it is reflected as a tension wave. If the tension waves becomes large enough and exceeds the ultimate strength of the material, fracture or spallation at the free surface could occur [94]. With the obtained results, probably, both mechanisms are involved.

Finally, HA films deposited on Ti or TiAl$_6$V$_4$ by PLD by using a hot substrate at a temperature between 400 °C and 800 °C (maximum value at which HA can be growth without chemical decomposition) can be deposited with grains of the order of 15 µm or larger, in our experiments. This is an useful improvement in the request of large photo-deposited HA grains in order to obtain irregular surfaces which promote the bone attachment.

4.3 **Pulsed Laser Deposition of Diamond-like Carbon**

The investigation of the carbon plasma is of special interest in the field of laser ion source (LIS), ion implantation, hadrons-therapy, and carbon nanostructure generation. The new ion sources generation uses LIS to
produce carbon extraction of $C^{1+}-C^{6+}$ beams; the ion implantation technique now can use the implant of multi-energetic carbon ions produced by laser-generated plasma in order to modify the chemical and physical properties of different surfaces; in the medical field, the hadrons-therapy is requiring more and more useful carbon ion beams to treat disease tissue; microelectronics and biochemistry are requiring instrumentation to generate carbon nanostructure aggregates and films for different aims [72].

In this work Pulsed Laser Deposition (PLD) technique has been employed to deposit a diamond-like carbon (DLC) film on different substrates of biomedical interest (Ti, Ti-alloys, SiO$_2$ and AISI 316L).

Coating materials with adherent graphite, diamond and DLC (diamond-like carbon) films provides specific applications as orthopaedic implants, cardiovascular components, guide wires, catheters, bypass conduits, drugs delivery, surgical instruments, dental filling points etc. In this field, among other coating materials, DLC emerges as a superior one in terms of smoothness properties, resulting much lower wear of a softer surface. On a well-prepared substrate, DLC can be atomically smooth, with roughness lower than 1 nm. In particular, as regards dental implants as well as massive metal implants, deposited DLC film results in good adhesion and, because of its dense structure, acts as a barrier preventing diffusion of the metal from the implant. In particular, fig. (4.14) [30] shows the EQP ion energy distribution as a function of the charge state at high laser energy. The high energy of the carbon ions justifies the implant in the first layers of the exposed surface producing high film-substrate adhesion and carbon nanostructure aggregates.
Further advantages of DLC are its mechanical resistance properties, hemocompatibility, thrombogenicity, and interactions with blood platelets. Tests performed on DLC coated titanium substrates produced no hemolytic effect, platelet activation, or tendency towards thrombus formation \cite{73}. Cell response to HA and DLC surfaces studies are of great interest since new products, using nanostructure and porous materials, can be employed with success in many prostheses implanted in vivo without harming or disrupting their intracellular molecular dynamics. Of course, the possibility to obtain porous HA and DLC materials with different grain size and high adhesion places is very important.

The set-up of the experimental apparatus necessary to Pulsed Laser Deposition technique has been widely discussed in the previous paragraph. Here we will discuss experimental results on the base of surface analysis of the photo-deposited films.

The fig. (4.15) \cite{91} reports two SEM images of a layer deposited on SiO$_2$ surface (1200 nm thickness), at $\varphi =0^\circ$ angle and $d =8$ cm target-substrate
distance. The inset of fig. (4.15.a) reports a design of the possible texturization of the thin film. The average DLC crystal size parameter is 300 nm. The shape of typical DLC crystals is cubic-like with rounded edges.

![Fig. 4.15: SEM image of C-film deposited in vacuum at 8 cm distance on the SiO$_2$ substrate placed at 0° and design of the possible texturization (a) and clusters observed at higher magnification (b).](image)

Sometimes the crystals have a tetragonal or rhomboidal shape, always with rounded corners. Using the dimension of the diamond unit cell ($a = 0.3567$ nm), in which each atom is tetrahedrally bonded with four neighbouring atoms, the number of unit cells composing the average volume of the observed structures is $1.4 \times 10^9$ and the corresponding number of contained C-atoms is $1.6 \times 10^{10}$.

Micro-Raman spectra obtained analyzing the DLC crystal cluster agglomerations give fundamental information about the molecular structure of the crystals, indicating that both sp$_2$ and sp$_3$ bonds are present. All the spectra show the characteristic graphite main peaks at approximately 1340 cm$^{-1}$ and 1530 cm$^{-1}$, usually referred to as D and G band, respectively [74, 75]. The figure (4.16) [91] reports the results of the Raman spectroscopy related to the analysis of carbon films deposited at 14 cm target-substrate distance and at different deposition angles. It is evident that the D and G structures are present only at little $\Phi$ angles with respect to the normal to
the target direction, while spectra typical of rich amorphous phases are detected at large deposition angles. Results indicate that at 0° and for little deposition angles, below 15°, the structure of the carbon crystals is well defined and rich of sp² and sp³ chemical bonds with respect to the glassy carbon target.

Fig. 4.16. (a) The results of the fitting procedure on the Raman spectra, for the Φ=10° case, showing the D- and G-peaks and (b) the typical micro-Raman spectra of photo-deposited films on SiO₂ surface placed at different Φ angles and at d=14cm.
A significant wavelength shift of the D peak from 1341 (glassy carbon) to 1386 (PLD film) cm\(^{-1}\) and of G peak from 1580 to 1533 cm\(^{-1}\) indicates that the carbon structure becomes more ordered. Moreover, the calculated lower value of \(I_D/I_G\) as the deposition angle decreases, suggests the existence of a more ordered structure for the crystal deposited near to the normal to the target direction. At large deposition angles, higher than 15°, the films contain only amorphous phases showing also here as the angle of deposition is a critical parameter.

The high energies of the ejected atomic and molecular species from the plasma and their high mobility on the substrate surfaces may produce effects of molecular recombination and clusters and nucleation formation. The evidence that the DLC films are nanostructured, showing characteristic Raman peaks and nanocrystals, demonstrate the high potentiality of the PLD technique in the deposition of biocompatible thin films. The low vacuum conditions is one of the condition that may favour the velocity growth, producing bigger crystals with respect to the case of high vacuum. This means that the residual gases may play important roles for the mobility of species on the substrate surface. The calculated lower value of \(I_D/I_G\) as the deposition angle decreases indicates the existence of a more ordered structure along the target-normal direction.

In conclusion, results obtained by DLC Raman spectroscopy and the comparison of these spectra with literature data [95] indicate that diamond-like nanocrystals have been deposited on the silicon oxide surfaces.
4.4 Superficial modifications induced by laser irradiation

In this section an ultra high molecular weight polyethylene (UHMWPE) mixed to carbon nano-tubes was investigated before and after the visible laser irradiation in vacuum. The aim is that one to improve some chemical and physical properties of the polymer and to obtain a sort of anisotropic polymeric sheet useful for different applications.

As we know energetic pulsed lasers are capable to induce modification and micromachining in different polymeric materials with submicron precision without incurring thermal damage to the surrounding unirradiated regions. With the short impulses of high intensity UV, visible and IR light provided by the laser, ablative photo-chemical and photo-thermal effects can be induced in the superficial layer of irradiated material producing high density of chemical bond scissions and cross-linking and outgassing of volatile species [110-112].

A special attention is devoted to the processes improving the polymer properties such as hardness, chemical and mechanical resistance and anisotropy. The laser ablation of hydrogenated polymers is a function of the deposited energy and that the ablation yield depends on the material absorption coefficient at the used incident laser wavelength.

The mechanisms responsible of the ablative photodecomposition of the irradiated polymer are the photochemical and photo-thermal involved effects. Depending on the properties of the irradiated material and the irradiation conditions, such as wavelength and pulse duration, one of them may become dominant. Generally, photochemical ablation occurs when incident photons have enough energy to bring the molecule in the excited electronically state, directly breaking main chain bonds. Energy absorbed in this bond-breaking process would restrict the temperature rise and the extent of thermal damage to the substrate. Instead, generally, the thermal ablation occurs when the incident single photon energy is not sufficient to
break a single chemical bond. In this case polymer chains bond breaking occurs for collective photon-molecule interactions \[113\]. Thermal processes can produce effective polymer ablation in which the photons couple to vibrational modes.

The employed laser in this work was a Nd:YAG operating at 532 nm (second harmonic) with 3 ns pulse duration, a maximum pulse energy of 150 mJ and a repetition rate of 10 Hz. The laser beam interacts with the target surface into high vacuum chamber (10\(^{-7}\) mbar) with a laser spot of 1.4 mm\(^2\) and 2 mm\(^2\), respectively. The laser pulse energy was changed from 10 mJ up to 150 mJ, which corresponds to a fluence ranging from 0.5 to 7.5 J/cm\(^2\) when the incidence angle was 45\(^\circ\), and a fluence ranging from 2.0 to 12 J/cm\(^2\) when the incidence angle was 0\(^\circ\).

The laser targets used in this work were a pure UHMWPE sheets and UHMWPE/CNT nano-composites whit carbon nano-tube (CNT) weight content between 0.5\% and 1.0\% (named respectively UH0.5CNT and UH1.0CNT). Their surface geometry was of 2 x 2 cm\(^2\) and 1 mm thick.

Surface morphology was investigated through a scanning electron microscope (SEM), carried out with a Jeol JSM 5600 LU microscope by employing a secondary electrons detector. The used acceleration voltage was of 20 kV and the photo magnification ranged between 50x and 10.000x. Roughness and hardness were determined with a Profiler Tencor-P10 by using a diamond tip force of 1,81 N, a scanion length of 1 mm, and a scan speed of 100 \(\mu\)m/s, at room temperature \[114\]. Hardness values were measured with respect to the hardness value of pure and non-irradiated UHMWPE obtaing relative hardness values. Contact angle measurements (CAM) were performed by depositing on the sample surfaces a 1\(\mu\)l of pure distilled water, at room temperature (20\(^\circ\)C) \[115\]. The drop was observed by a small CCD camera and a suitable PC images treatment software. Transmission infrared spectra (FTIR) were performed on about 300 \(\mu\)m
thick films of nanocomposite and registered by a Perkin Elmer Spectrum 2000 instrument equipped with a MCT detector in the 600-4000 cm\(^{-1}\) wave-number region [116]. Finally, measurements of electrical resistance until 20 M\(\Omega\) of the three kinds of polymers were performed using polymeric sheets with know geometry (disks with 9 mm in diameter and 1 mm thick) with a digital tester ISO-TECH IDM91E.

Fig. (4.17) [117] shows the visible effects of laser irradiation on studied materials. In particular, fig.(4.17.a) shows a photograph of an UHMWPE sheet which appears semi transparent with a light yellow coloration in the irradiated area (signed with a colored pen).

![Photographs of UHMWPE (a), UH0.5CNT (b) and UH1.0 CNT(c) irradiated for 120 seconds. SEM micrographs of CNT before laser irradiation with magnification of 10,000x (d) and after laser irradiation for 15 seconds with magnification of 1,500 x (e).](image)

Figs. [(4.17.b), (4.17.c)] show the black sheets of UH0.5CNT and UH1.0CNT nano-composite; the laser irradiated areas of both these samples appears white and opaque. Fig. (4.17.d) shows the SEM
micrograph of pristine CNT. The following irradiation at 100 mJ laser energy for 15 s, fluence of 2.4 J/cm$^2$, produces a significant compacted material showing grains knit and grains fuse between of them, as reported in fig. (4.17.e). This compactness increases with the irradiation dose, i.e. with the laser irradiation time and pulse energy.

Figure 4.18 – SEM micrographs of UH0.5CNT and UH1.0CNT surface (top view) laserated for 120s with magnification of 150x (a,b); the frontal view of their modified layer at 50x (c,e) and relative magnification at 150 x (d,f).
Fig. (4.18) [117] shows a lot of SEM micrographs of the nano-composite after the laser treatment for 120 s with 170 mJ laser pulse energy, fluence of 12 J/cm², at 50x or 150x magnifications. The laser irradiation induces a morphology strongly dependent on the nano-tube concentration. Increasing this parameter, the irradiated polymer appears more uniform in surface. At low nano-tube concentration (UH0.5CNT sample) the polymer contains high density of voids and appears so as large grains of polyethylene with dimensions of the order of 100 µm and deeper grain contours (fig. (4.18.a)). At high nano-tube concentration (UH1.0CNT sample) the polymeric surface appears uniform, without voids and grain contours, similarly to the surface of UHMWPE pure pristine (fig. (4.18.b)) [114].

The polymer modifications due to the laser irradiation at high dose are mainly due to the removing of superficial nano-tubes and fusion of them. The first effect can be due mainly to electrical forces on the charged nano-tubes and charged polyethylene matrix, caused by photon ionization processes, which produces distach of entire nanostructures from the polymer surface. The second effect can be due to the high temperature produced by photo-thermal effects induced by the energetic laser pulse at laser fluence of 12 J/cm², which generate vaporization of the nano-tube and of the surrounding polymeric zone.

Laser modification concerns only the superficial region of the irradiated polymer, up to a depth of about 160-200 µm, as shown by the SEM micrographs of the UH0.5CNT [figs. (4.18.c), (4.18.d)] and UH1.0CNT samples [figs. (4.18.e), (4.18.f)] in lateral view, along their thickness. The images show irregularities and voids on the surface whose depth depends on the absorption coefficient at 532 nm of the UHMWPE mixed to carbon nano-tube structure. Thus the laser treatment produces an anisotropic polymer which surface, up to about 200 µm depth, is very different from
the bulk. In order to characterize the properties of the new treated polymer, different measurements have been done.

Fig. (4.19.a) [117] shows the hardness values as a function of the irradiation time of the UHMWPE, UH0.5CNT and UH1.0CNT samples.

Fig. 4.19. Relative hardness (a) and roughness (b) of UHMWPE, UH0.5CNT and UH1.0CNT samples as a function of the irradiation time.

Fig. 4.19. Relative hardness (a) and roughness (b) of UHMWPE, UH0.5CNT and UH1.0CNT samples as a function of the irradiation time.
The surface hardness was measured with a profile tip, which has the typical shape reported in the figure inset. Results indicate that the nano-tube presence increases the polymer hardness. The following laser irradiation of the nano-composite, producing nano-tube detachment, decreases it. At irradiation times higher than 50 s, hardness becomes lower than in the pure UHMWPE.

Fig. (4.19.b) reports the results of the roughness measurements in the same three samples above mentioned. Roughness, which a typical spectrum is reported in the figure inset. It is very low in the pure UHMWPE, where it remains unchanged after high dose laser treatment. It increases with increasing the nano-tube content and the irradiation time.

Fig. (4.20) shows the wet ability and the electrical resistance values versus the irradiation time of UHMWPE, UH0.5CNT and UH1.0CNT samples.
Fig. 4.20. Contact angle (a) and electrical resistance (b) of UHMWPE, UH0.5CNT and UH1.0CNT samples as a function of the irradiation time.

The contact angle values (fig. (4.20.a)) decreases with increasing the nanotube content in the polymer. Moreover, the contact angle of the pure UHMWPE and of the UH0.5CNT decreases with the irradiation time while it increases in the UH1.0CNT sample. Finally, the surface electrical resistance measurements, presented in fig. (4.20.b), indicate that the
polymer resistivity decreases in the high nano-tube doped polymer. It decreases also using low laser irradiation times of doped polyethylene, lower than 30 s. High doses of laser irradiation, remove and/or melt nano-tube the surface, i.e. the sites responsible of the electrical conduction, induces a film resistivity stabilization.

The FTIR spectra of UH1.0CNT irradiated at different exposition times (0-30-60 s are presented in fig. (4.21).

![FTIR spectra of UH1.0CNT](image)

**Fig. 4.21.** FTIR analysis of UHMWPE, UH0.5CNT and UH1.0 CNT samples irradiated for 120 seconds.

No any qualitative difference can be detected by the peaks presented in the spectra. This result confirms that laser irradiation effect consists on a carbon nanotube removing and/or melting process on the surface since this recombination type does not change the chemical bond type and amount on the material surface.

Finally, fig. (4.22) shows the scheme of a hypothetical “sandwiches” made by lasering the nanocomposite sheet on both the sides. This new anisotropic material shows different properties on its surface compared
with the bulk. In particular the surface has a high roughness, hydrophilic properties, low hardness and insulator properties. The inner part, vice versa, is electrically conductive, hard and hydrophobic.

Fig. 4.22. Scheme of nanocomposites cross section modified by laser irradiation.

By this investigation we can deduce that because pure UHMWPE has a low light absorption coefficient at 532 nm wavelength, negligible modifications can be induced by its laser irradiation. At high dose the polymer shows only a little change of its coloration and wet ability. No other appreciably changes, like roughness, hardness or morphology were noticed.

More significant changes, instead, occurred in the carbon nanotube structure. At high dose the CNT filaments show melting, due to the thermal energy of the irradiation process. This phenomenon suggested that carbon nano-tubes adsorb the laser irradiation and appreciably it changes, both at low and high dose.

Laser effect in the nanocomposite depends on the carbon nanotube amount present in the material and on the irradiation time. Laser effect involved, anyway, only the external layers of nanocomposite, leaving the bulk unchanged. Nano-tube presence modifies the pristine polymeric properties increasing its hydrophilic character, decreasing its electrical resistance and, generally, increasing the material laser adsorption coefficient.
Two main effects were induced by the laser irradiation on the nanocomposite surface. They involved principally the carbon nano tubes and partially the polymeric matrix. It was hypotized that carbon nano-tube melting and/or removing process could be happen on the nano composite surface. Furthermore, these processes could result in a physical or chemical new bonds formation between the carbon filaments and /or the polymeric matrix.

This new re-organization of the carbon-carbon or carbon-hydrogen bonds and/or the formation of the physical interactions (like Van de Waals or polar bonds) results in a global unchanging of the total C-C or C-H bonds.

The nanocomposites change the UHMWPE surface morphology showing an higher roughness and lower hardness since great holes and anisotropies are enclosed. These surface modifications increase with the CNT amount and with the irradiation times.

At the highest irradiation times (120 s), nanotube removal prevails at low CNT amounts (0.5 wt%), while both CNT remove and CNT melting occur at higher CNT amounts (1.0 wt%). The color changing, observed in the samples before and after the irradiation, suggests that the main laser effect consist on the CNT removing. This effect changes the external layer that results more similar, but no identical, to the pure UHMWPE. New polymeric structure rearrangements and /or CNT-polymer melting process cannot be excluded. Further investigation should be performed in a following research work in order to better discriminate among the possible materials reorganization processes.

The nano composites wet ability increased or decreased depending on the nano tube content. This effect was more pronounced at high laser exposition times rather than lower ones. The hydrophilic properties of the laser irradiated nano composites were not well correlable with the
macroscopic surface change induced by the irradiation. In this case, physical polar or Van der Waals interactions induced on the polymeric surface, could greatly influence its wet ability.

The high electric conductivity in UHMWPE polymer mixed to nanotubes can be due to the ability of electron tunnel effects between the conductive nano-isles enclosed in the insulator matrix. The enhanced conductivity due to the laser irradiation can be due to the enlargement of the isle dimensions due to the CNT fusion in the target and to the increment of carbon vapor deposition on the treated surfaces.

Concluding, the UHMWPE polymer can be treated efficiently by pulsed laser irradiation in vacuum, in order to modify the superficial properties of the polymer without change the bulk ones. Increasing the laser energy and/or the irradiation time it is possible to modify significantly the properties of pure UHMWPE and nano-tube doped polyethylene up to a depth of about 200 microns.

The superficial layer, with respect to the pristine one, shows a different morphology, more hard, more roughness, and with different wetting ability, depending on the content of nano-tube in the polyethylene and the irradiation dose.

Irradiating both the faces of a polyethylene sheet, of few mm in thickness, it is possible to produce an new anisotropic polymer structure which surface properties are different from the bulk. This new material may find interesting applications in engineering, microelectronics, biomaterials, etc., due to its special physical and chemical, surface and bulk, properties.
5 Laser Ion Source for Ion Implantation

5.1 Introduction to ion implantation

Ion implantation is a powerful tool that can improve the physical and chemical properties of different substrate materials. The first junction in a semiconductor was successfully produced by ion implantation in the year 1954 when W. Shockley [96] took out his patent for “forming semiconductive devices by ionic bombardment”. Today the ion implantation has achieved a wide application in the semiconductor industry because of the possibility to alter the conductivity of the material of several orders of magnitude by introducing small quantities of dopant atoms, for the ability to control the number of implanted dopants and the possibility to place them at the desired depth.

Ion implantation is also used as surface modification process in which ions are injected into near-surface region of a substrate. With this process, properties such as hardness, wear resistance, corrosion resistance, resistivity, elastic modulus and fatigue resistance may be altered according to the selected implantation element. High-energy ions, typically 10-200 keV in energy, are produced in an accelerator and directed as a beam onto
the surface of the substrate. The ions impinge on the substrate with kinetic energies 4-5 orders of magnitude greater than the binding energy of the solid substrate and form an alloy with the impact surface. Generally, the implanted substrates include metals, ceramics, and polymers. The most commonly implanted metals include steels, titanium alloys, and some refractory metals, while implanted polymers include polyethylene at ultra high molecular weight (UHMWPE) for his wide use in different fields.

In order to compare the ion implanters traditional with a new type of implanter, called Laser Ion Implanter (LII) and in project near INFN-LNS of Catania, we will describe in schematic way the principles of functioning of a traditional implanter referring to the literature for further explanations.

An implanter is basically an ionic accelerator constituted by ion source, a system of post acceleration and focusing and a support for the samples to implant. Operations happen in succession where the ions are produced into source, extracted and accelerated to the energies required.

One of the first ion sources used for ion implanters was the so called Radio Frequency source (RF source), where a high frequency field, 150 MHz, was used between two plates to ionize the gas. This source was soon discarded because of relatively small current and contamination of the source envelope. To replace the disadvantages of the RF source, was introduced the hollow cathode Penning discharge source where two electrodes, a cup-like cathode and a cylindrical anode are maintained at high voltage, 2±4 kV, to create an arc when gas is introduced between them. This process forms dense plasma from which the ion beam is generated. The continuous development and research in the ion implantation field has produced ion sources of higher current and maybe the most versatile ion source for implanters is the hot cathode arc discharge ion source developed by Freeman, shown in fig. (5.1). In this source a cathode of tungsten is heated to the right emission temperature,
usually higher than 1200 °K, that causes an electron flow from cathode to anode.

Electrons emitted by the cathode are attracted by the positive voltage of the anode, collide with gas molecules and ionized them creating a beam of positive ions. To increase the path of the electrons from cathode to anode and hence the probability of collisions, a magnetic field perpendicular to the travel path of the electrons is introduced. In this way the most of the atoms entering into arc-chamber will be ionized. Successively, a magnet field divides the beam in much part how much are the atomic masses or molecular present. Finally comes isolated the beam containing the ionic species desire and send to the samples-holder system. Fig. (5.2.a) and fig. (5.2.b) show a scheme of ion implanter traditional where the acceleration system is positioned before and then the filter magnet, respectively [97].
In this introductory paragraph we have given greater emphasis to the ion source because the innovation of the new ion implanter, i.e. Laser Ion Implanter, lies into ion source.
5.2 Laser Ion Implanter

The laser ion sources (LIS) represents a new reality in the field of the ion generation with high efficiency, high charge state and high kinetic energy [98]. Produced ions can be employed in different way, from the ion injection in accelerators to the improvement in pulsed laser deposition of thin films. A new idea of use of ions laser produced concerns their employment in the field on the ion implantation. Such ions, having different charge state, large range of kinetic energy (from eV to keV), Boltzmann-shifted energy distributions, high total current density, can be accelerated and focused in order to obtain multi-energetic ion beams with energies of the order of hundred keV, useful for ion implantation processes [3, 79].

This work is a preliminary investigation in the employment of LIS ions for multiple ion implantations. These implants modify significantly the chemical and physical properties of different material surfaces in a layer thickness depending on the range of the impinging ions. Changes in composition, hardness, wear, wetting, chemical inertia, surface morphology etc. represent same examples of surface modifications induced by high implanted ion dose [99, 100]. Multiple ion implantation finds interesting applications in microelectronics, bio-engineering and metallurgy.

In this study a Laser Ion Implanter (LII) is employed to produce non-equilibrium titanium plasma, where the new source is obtained with a pulsed Nd:YAG laser operating in the power density region of $10^{10}$ W/cm$^2$, with a wavelength of 1064 nm, a pulse duration of 9 ns, and a maximum pulse energy of 900 mJ. The repetition rate was 30 Hz. The laser light was focused on the solid target of titanium situated in a vacuum chamber at $10^{-6}$ mbar pressure with a Gaussian spot variable from 0.5 to 1 mm$^2$. The incident angle respect to the normal of the surface target was 45°. The Boltzmann ion energy distributions were measured through an electrostatic
ion energy analyzer (IEA) mounted along the normal to the target surface, which permits to detect the kinetic energy and the charge states of the ions ejected from the plasma [21]. In fig. (5.3) is shown the scheme of the

![Scheme of the experimental set-up performed with TOSCA computer simulation.](image)

Fig. 5.3. Scheme of the experimental set-up performed with TOSCA computer simulation.

simulated experimental set-up. The distance from target and the diaphragm-radius of the deflector has changed in the course of different simulations to optimize the ions trajectories from target source to the substrate. In order to accelerate the ions towards the substrate, the target has been polarized positively while to focalize the beam has been used a magnetic field.

How ion source has been taken the Ti ion energy distribution, shown in fig. (5.4) [122], where one titanium target is irradiated at high laser fluence. The plasma contains ions at high energy and high charge state (up to $5^+$) as shown in Table (5.I).
Fig. 5.4. Experimental Ti ion energy distribution

<table>
<thead>
<tr>
<th>Charge State</th>
<th>Average Kinetic Energy (eV)</th>
<th>Average Velocity (x10^4 m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti^{1+}</td>
<td>600</td>
<td>4.9</td>
</tr>
<tr>
<td>Ti^{2+}</td>
<td>900</td>
<td>6.0</td>
</tr>
<tr>
<td>Ti^{3+}</td>
<td>1150</td>
<td>6.8</td>
</tr>
<tr>
<td>Ti^{4+}</td>
<td>1400</td>
<td>7.5</td>
</tr>
<tr>
<td>Ti^{5+}</td>
<td>1700</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Tab. 5.I: Typical ion distribution obtained by Laser Ion Source.

This experimental ion energy distribution has been taken like input data initial for the simulation of the ions trajectories.
A first simulation regards the reproduction of the experimental ion energy distribution with MATLAB computer program, fig. (5.5),

\[
F(v_T, v_k, v_e) = A \left( \frac{m}{2\pi kT} \right)^{3/2} v_T^3 e^{-\frac{m(v_T - v_k)}{2kT}}
\]

where has been used the Boltzmann-Coulomb shifted distribution proposed by Torrisi et al. [26].

A second simulation regards the outlet angle of the ions from centre of laser spot on the target. The relationship that well adapt the experimental data is [6],

\[
D(\Theta) = A \cos^p \Theta
\]

(5.1)

where \( A \) is a normalization constant and \( p \) is an exponent that depends on the type of target. In fig. (5.6) we have a simulated angular distribution of neutral and ions emitted of Ti target irradiated at laser fluence of 100 J/cm\(^2\).
Fig. 5.6. Comparison of the simulated angular distribution of neutral and ions of Ti target.

The exponent $p$ assumes the values of about 22 and 8 for the ion and the neutral distribution, respectively [6]. The angle of emission of the ions, necessary for the simulations, has been in random way from 0 to $\pi/6$.

These simulations permit to calculate the initial velocity of ions and the angle of output respect to the normal direction of the surface target.

The average kinetic energy of the Ti ions (0.6 ÷ 1.7 keV) to the target source is too low to be implanted therefore the target has been positively polarized (+50 keV) in order to accelerate the ions towards the substrate, as shown in fig. (5.7). The cylindrical deflector and the substrate are connected to the ground.
Fig. 5.7. Action of the electric field on ion trajectories in the simulated experimental set-up.

In order to focus the emitted ions, has been introduced also a uniform magnetic field to variable values. The vector B is placed along the system axis. Fig. (5.8.a) and fig. (5.8.b) shows the action of magnetic and electric fields on ions trajectories.

\[ \vec{F} = q\vec{E} \]

Fig. 5.8.a. Simulation of the action of magnetic field of 1 Tesla and of the target polarized with 50 kV positive bias, on ion trajectories.
Fig. 5.8.b. Simulation of the action of magnetic field of 2 Tesla and of the target polarized with 50 kV positive bias, on ion trajectories.

The results above obtained can be reassumed in fig. (5.9) where the graph shows that the insertion of a magnetic field improves the ions current to the substrate. With the magnetic field of 2 Tesla a good ion beam focalization can be obtained and the percentage of ions on 4 cm$^2$ substrate implanted area increase up to 83%.
The ion beam obtained in such a way has a total ion current of about 1 mA over five ion charge states with different intensities. In this way, the substrate will be submitted to a multiple implantation with ions having average energy from about 51 keV up to about 252 keV for Ti$^{1+}$ and Ti$^{5+}$, respectively.

SRIM (Stopping and Range of Ions in Matter) is a computer program that has been used to calculate the stopping and range of ions in matter. The SRIM simulations of the Ti ions produced by laser ablation, accelerated by target polarized at +50 kV, and implanted on Al substrate have been performed by using the relative ion abundance experimental measured [122] and shows in Tab. (5.II).
<table>
<thead>
<tr>
<th>Element</th>
<th>Acceleration Voltage (kV)</th>
<th>Average Kinetic Energy at the Target (keV)</th>
<th>Ion Energy at the substrate (keV)</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{1+})</td>
<td>50 kV</td>
<td>0,6</td>
<td>51</td>
<td>42</td>
</tr>
<tr>
<td>Ti(^{2+})</td>
<td>50 kV</td>
<td>0,9</td>
<td>101</td>
<td>26</td>
</tr>
<tr>
<td>Ti(^{3+})</td>
<td>50 kV</td>
<td>1,15</td>
<td>151</td>
<td>15</td>
</tr>
<tr>
<td>Ti(^{4+})</td>
<td>50 kV</td>
<td>1,4</td>
<td>201</td>
<td>11</td>
</tr>
<tr>
<td>Ti(^{5+})</td>
<td>50 kV</td>
<td>1,7</td>
<td>252</td>
<td>6</td>
</tr>
</tbody>
</table>

Tab. 5.II: Typical ion distribution and relative ion abundance obtainable by Laser Ion Source.

Fig. (5.10) shows the ions energy vs. target depth for different charge states and ions energy to the surface of the substrate (E\(_S\)).
Fig. 5.10. Ions energy vs. target depth for Ti\(^{1+}\) at 51 keV (a), Ti\(^{2+}\) at 101 keV (b), Ti\(^{3+}\) at 151 keV (c), Ti\(^{4+}\) at 201 keV (d), and Ti\(^{5+}\) at 252 keV.

Fig. (5.11) shows ion ranges and depth profile for different charge states and ion energy to the surface of the substrate. The relationship on axis of ordinates, (atoms/cm\(^3\))/(atoms/cm\(^2\)), shows the impurity concentration in terms of (atoms/cm\(^3\)) vs. target depth. When this quantity is multiplied for the ions dose, (ions/cm\(^2\)), from implant, one gets the concentration of impurity.
The final Ti depth profile, reported in fig. (5.12), due to the convolution of different ion energy depositions, demonstrates that ions are implanted into substrate up to depth of the order of 340 nm.
In conclusion we can say that the aim of this work is to realize a new kind of ion implanter, with ions energy range from 51 keV to 250 keV which permits multiple ion implants together on a given substrate surface. A LIS is employed as ion source for its easy operation, high ion current emission and high directivity of ion emission.

The computer simulations reported in this work represents a preliminary tentative to fix some parameters of a simple and compact implanter accelerator. The proposed accelerator may find important applications in the field of ion implantation of metals, semiconductors, ceramics and polymers’ surfaces, which can be chemically and physically modified by high ion dose implantation. For example hardness, chemical reactivity, roughness, wetting ability, wear resistance, electrical
conductivity and density of the implanted layers can be modified at doses of the order of $10^{17}$ ions/cm$^2$ for metals and of the order of $10^{15}$/cm$^2$ for many polymers [101]. Due to the multi-energetic ion beams and to the high ion current (~ 1 mA), these accelerators may reach the requested doses and the requested implant depth profiles faster than the traditional mono-energetic ion beams at low currents (~ 1-10 $\mu$A), which need multiple energy modifications to get multiple ion depth profiles in the substrate. By varying the range, it is also possible to obtain a thick surface layer with special properties.

Unfortunately the laser ion source produces not only ions but also neutrals and clusters, two species that will be deposited on the substrate, during the ion implantation, as a thin coverage film. For special applications this high neutral component is unacceptable. Further investigations, employing different set-up geometries, are in progress in order to reduce the percentage of neutrals and clusters’ deposition on the implantable substrate surface.

5.3 **Superficial modification by multi-ion implantation in UHMWPE**

New devices made of polyethylene at ultra high molecular weight (UHMWPE), are employed in different fields (mechanics, medicine, chemistry, food industry, pharmaceutical industry, transport, vehicles, etc.) for its excellent chemical and physical properties. In medicine, for instance, UHMWPE is employed in many prosthesis devices such as in the artificial knee and hip joints and in the vertebral rings and for orthopedic screws\(^1\). This material has a high degree of homogeneity, high mechanical stability and good elastic properties similar to the hard tissue and the bone [102-104].

Unfortunately, UHMWPE, if submitted to high mechanical dynamical stresses, to high temperature and to high corrosive environment,
it suffers alterations. Special attention is devoted to the UHMWPE wear as a result of friction against hard surfaces at body temperature. This wear, typically for polyethylene employed in many mobile prostheses, is characterized by different polymeric alterations such as elastic loss, weight loss, change of density, permeability, surface roughness, chains fractures, small and large grains loss, hardness increasing and polymer aging. Therefore, it is interesting to investigate the chemical and physical processes which can improve the UHMWPE wear resistance. Generally, the problem involves the polyethylene surface, and it need to be reinforced by the polymeric surface layers so that the friction wear can be reduced and the whole device lifetime increased [105]. An improvement of the wear resistance of UHMWPE can be obtained by using a new ion implantation technique induced by laser-generated plasma at high ion dose. Indeed, the ion implantation technique is a process in which accelerated ions are directed toward a substrate at energies high enough to penetrate just below the substrate surface without causing damage to the lattice but modifying the target properties and improving the mechanical, thermal, electric and optical properties.

The laser ion source (LIS) technique produces high doses of ions per laser pulse, up to $10^{14}$ ions/cm$^2$, and it has the advantages to work at low temperature and to allow multiple ion implants together on a given substrate surface. Laser-produced plasma generates ions that can be accelerated by means of an external electric field and implanted in a given substrate as we have seen in the previous paragraph. In this work, to show the feasibility of ion implantation via LIS, was employ a DC electric field for ion extraction and acceleration. In order to operate at high ion doses the electrostatic accelerating voltage for implantation of polyethylene was chosen ranging from 20 to 30 kV.
The ions source is obtained with a KrF excimer laser operating at 248 nm wavelength (5 eV photon energy) with a laser energy of 70 mJ/pulse that providing a laser fluence of about 7 J/cm$^2$ and a power density of 3.5·$10^8$ W/cm$^2$. The laser beam was focusing with a lens forming a spot of about 0.01 cm$^2$ on the surface of the target.

As shown in fig. (5.13) [106], the implantation chamber consisted of a plasma generation chamber (GC), 26.5 cm long, and a removable expansion chamber (EC), which allows an initial free expansion of the plasma before the ion extraction. The target support was a stem (2 cm in diameter) mounted on the GC by an insulating flange (IF) and kept to positive high voltage, in DC mode. A grounded electrode (GE) in front of the EC allowed either to generate an intense electric field or to support the substrate to be implanted. Such an arrangement presents the advantage to apply a uniform electric field even for no-conductor substrates. A set of four buffer high-voltage capacitors, each of 1 nF, was connected between the target stem and the GE to stabilize the voltage during the extraction process. In such a way the capacitor-stored charge was much higher than the extracted one, maintaining constant the accelerating voltage value.

The EC was indispensable to avoid arcs. It is an almost hermetic cylinder, 18.5 cm long, 9.0 cm in diameter, having the hole (1.0 cm in diameter) necessary for the ion extraction worked on its basis-electrode.
With this experimental set-up, the implantation zone area was 0.78 cm$^2$. A 99.99% pure carbon and a 99.99% titanium were used as the laser beam target, in the form of a little thin disc. It was suitably rotated during the implantation process in order to avoid the formation of a unique crater decreasing the ion emission yield. The laser was operated at 1 Hz repetition rate. The vacuum chamber was evacuated by a turbo-molecular pump down to $10^{-6}$ mbar.

The implanted substrate were three samples of polyethylene: two samples with C and one Ti ions. Knowing the ion concentration at the laser fluence of 7 J/cm$^2$ of $1 \times 10^{11}$ ions/cm$^2$, we calculated the dose implanted. In table (5.III) [106] all the studied samples and the relative treatments are resumed.
The surface morphology was investigated through a SEM, carried out with a Jeol JSM 5600 LU microscope, in order to evidence eventual differences before and after the UV pulsed laser irradiation. The samples were coated in vacuum with a very thin gold film to make them electrically conductive. The analysis was performed by employing a secondary electrons detector. Generally, the acceleration used voltage was of 20 kV and the photo magnifications were 200x.

The roughness was determined with a Profiler Tencor-P10 which moves a micrometric point along a single direction and the scansion is assisted “on line” by an optical microscope. Measurements were performed in different places of the same surface and average values were calculated by using a tip force of 1 mg, a scansion length of 1 mm, and a scan speed of 100 µm/s. [107].

The hardness of surface was performed by applying the “scratch test” method. The scratch tests were performed with a diamond tip producing a scratch due to 30 gr perpendicular force measuring the scratch width.

The wettability was performed by the contact angle measurement. It was carried out according to the sessile drop technique and performed by the contact angle micrometer [108]. A micro-syringe was employed to deposit 1 µl drop of distilled water (at 20 °C temperature) on the polymer surface. The contact angle $\theta$ was measured by a CCD camera through the optical image (10x magnification) and it was measured with the following equation:

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Deposited Ion</th>
<th>Energy (kV)</th>
<th>Dose (ions/cm$^2$)</th>
<th>Number Laser shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>UH</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UHC1</td>
<td>C+</td>
<td>30</td>
<td>5x10$^{13}$</td>
<td>500</td>
</tr>
<tr>
<td>UHC2</td>
<td>C+</td>
<td>20</td>
<td>2x10$^{14}$</td>
<td>2000</td>
</tr>
<tr>
<td>UHTi</td>
<td>Ti+</td>
<td>20</td>
<td>2x10$^{14}$</td>
<td>2000</td>
</tr>
</tbody>
</table>

Tab. 5.III: Modification parameters of the UHMWPE samples.
\[ \theta = 2 \arctan \left( \frac{H}{r} \right) \]

(5.2)

where \( H \) is the height of a droplet and \( r \) is the radius of the droplet’s base.

For each sample, the average value was calculated for 10 drops measurements. The contact angle \( \theta \) relative to the non-wetting case is \( >90^\circ \) and the one to the wetting case is \( <90^\circ \).

Also in this section has been used SRIM computer program [109] in order to calculate the ion penetration range produced by the pulsed UV laser when the ions beam irradiates the UHMWPE. Fig. (5.14) shows a Monte Carlo simulation of the ion tracks in a polyethylene bulk sample obtained with SRIM program of Ziegler. By simulation of 20 keV C and Ti ions we have a maximum range of penetration in UHMWPE of about 150 and 80 nm, respectively [106].

![Fig. 5.14. Monte Carlo simulation of the 20 keV ion range distributions in a polyethylene bulk sample.](image)

Fig. (5.15) [106], shows the contact angle pictures relative to the UHC1, UHC2, UHTi, ion implanted samples. The pictures indicate an increasing of the wet ability at different implanted doses.
As summarized in Table (5.IV) [106], the contact angle value is lowest for the UHTi sample (c) (Ti implant) and largest for UHC1 sample (a) (C implant).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\theta^\circ$</th>
<th>Roughness ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UH</td>
<td>69.3</td>
<td>45</td>
</tr>
<tr>
<td>UHC1</td>
<td>71.3</td>
<td>40</td>
</tr>
<tr>
<td>UHC2</td>
<td>67.5</td>
<td>35</td>
</tr>
<tr>
<td>UHTi</td>
<td>63.1</td>
<td>27</td>
</tr>
</tbody>
</table>

Tab. 5.IV: Wettability and roughness values of UHMWPE samples with respect to the untreated sample called UH.

The surface roughness values, measured by the Tencor surface profiler, are also reported. It has been proved experimentally that the surface roughness decreases the wettability of a hydrophobic material. From results of Table IV the wettability increases for the samples treated with high doses. The wettability of the UHC1 sample is nearly to the one of the HC but increasing the ion dose and the ion stopping power the wetting ability increases as demonstrated by the UHTi sample. We ascribe this result to the low implantation dose.
The SEM photos of fig. (5.16) [106] show a typical example of the test on the implanted surface (UHC2) at which the width is about 50 µm, fig. (5.16.a), i.e. 80% lower than in non implanted (UH) surface as shown in fig. (5.16.b).

Fig. 5.16. SEM photo of the scratch test. a) UHC2 sample; b) UH sample.
Therefore, the smaller scratch indicates a lower tip deep in the sample surface, i.e., that a little increment of the surface hardness occurred in the implanted samples.

In conclusion we can say that wear investigations of hydrogenated polymers indicate that the UHMWPE is most resistant to the friction against different materials (polymers, metals and ceramics) with respect to other un-treated PE polymers and that it is therefore a good candidate material to be employed in many devices, such as electrical insulator films and medical prosthesis joints, to damp mechanical stresses. The wear mechanism is mainly connected with the polymeric structure and, particularly, with its molecular weight and crystallinity degree. The high number of entanglements present in polymers of high molecular weight with a narrow distribution ties up the local mobility of the polymeric chains. This effect is much more pronounced if the polymeric material has a high crystalline degree or if it is cross-linked because its chain movements are even more strongly obstructed. These investigations show that the polymers dehydrogenation and high cross-link chains induced by ion implantation produces a surface more resistant to friction. These surfaces have many physical properties similar to graphite, a material very useful to be employed as a sheet between two mobile surfaces in order to reduce their friction. Moreover, the high carbon content increases the material biocompatibility and blood-compatibility giving more successful application to the material for prosthesis realization Ion implantation greatly modifies the polymeric surface and highly reduces its wear mechanism. The crystallinity degree decreases in the cross-linked implanted area suggesting that the wear mechanism reduction is mainly influenced by the presence of cross-links rather than by the degree of ordered chains. The “graphite-like” surface layers of UHMWPE are strongly adherent to the substrate because strong chemical bonding occurs.
The thickness of the layer can be changed by the ion beam energy (particle range) and the carbon content can be changed by the ion dose of irradiation. The non-irradiated substrate polyethylene does not change its chemical and physical properties.

Work is in progress to investigate further on the dependence on the stopping power and ion dose of the polyethylene properties.
CONCLUSIONS

The results reported in this work indicate that the use of the laser presents a variety of applications and a variety of experiments are possible.

In medical field, the major application of laser technology has been in ophthalmology, where the wavelength of the laser employed, absorption coefficient of the tissue, power density of the laser, and the duration of laser radiation are very important to control the laser-tissue interaction. Some three-dimensional simulations have been carried out in order to value the optical and thermal response of a biological tissue to the laser radiation. The aim was to minimize the thermal damage. Further investigations are in progress because the solutions of thermodynamic equations with computer simulations not adequately describe the thermal process, in some situations. While, excellent agreement between measured and computed temperatures have been reported for the eye [54]. The future of the laser in medical field is directed, principally, on photodynamic therapy (PDT), a therapeutic method requiring a drug (photosensitizer), a device (light source and light delivery device), and the presence of molecular oxygen for the treatment of a variety of human clinical conditions [137-139]. It is a two-stage process where the first stage consisting of the delivery of a photosensitizer, called PHOTOFRIN (QLT, Inc). Following a period of time during which PHOTOFRIN is mostly cleared from a variety of tissue (48-72 h) and retained in tumour, skin, and organs of the reticuloendothelial system (including liver and spleen). In the second and final stage of the therapy, the tumour is illumined with laser light at 630 nm and the presence of oxygen is required for PDT-induced target tissue destruction [137-139].

In dental field the ablation efficiency, thermal damage, and final surface characteristics are the ultimate test to any laser effectiveness. In particular Er,Cr:YSGG pulsed laser has been proposed as candidate for
efficient hard tissue ablation since its high absorption coefficient allows an
dlarge energy/volume deposition and minimal heat diffusion, which
improves ablation rates with minimal collateral thermal damage [57].
The results indicate that the ablation yield grows linearly with the laser
fluence and that the Er,Cr:YSGG laser induces higher ablation effects with
respect to other lasers, as result of the high absorption coefficient and the
use of the air-water integrated spray to the handpiece. The ablation yield
decreases if the two concentrations of water and air are different, while
increases when these two concentrations are similar.
These results confirm the validity of the HydroKinetic System (HKS)
technique where the hydrokinetic tissue-cutting refers to the process to
removing hard biological material through the use of high speed controlled
water droplets. Strong absorption of laser energy by fine water droplets
results in a violent yet controlled micro expansion inducing strong
mechanical forces on targeted tissue surfaces.
Laser wavelength, pulse width, wavelength-dependent absorption and
energy density are critical in determining the relative amount of ablated
material. Also, the water-air spray system determines the value of the
ablation yield, permitting to ablate dental tissue in normal environment and
contemporary to remove irradiated mass from the deep crater. Increasing
the laser fluence and the water and air flux spray, the ablation yield
increases.
Because the laser-target tissue interaction is dependent by hydrokinetic
tissue-cutting effect and probably an efficient ablation at a given parameter
set (pulse duration, pulse energy, spot size, etc.) does not proceed until
plasma is initiated, ulterior investigations on the role of plasma are
necessary.

In biomedical field, few are the biomaterial compositions that have
achieved human clinical application [68, 69, 70]. Clinical success requires
the simultaneous achievement of a stable interface with tissue and a match of the mechanical behaviour of the implant with the tissue to be replaced \[71\]. A this purpose, the Pulsed Laser Deposition (PLD) permits to deposite biomaterial coatings in vacuum preserving their original properties. The results of the investigations have shown that laser wavelength, pulse width and energy density are critical in determining the relative amount of material deposited both such as granular components and molecular component.

An important result regard the HA films deposited both on Ti and Si substrates using a Nd:YAG pulsed laser operating at 1064 nm, with short pulses of 9 ns duration a repetition rate of 30 Hz, and a laser fluence of 30 J/cm\(^2\). The average grain size was about 15 µm, a factor 5 higher with respect to those obtained in similar conditions by using the ruby laser \[80\]. This is a very important result because in this field of research the best method of HA deposition should give high granular films and porous films in order to optimize the surface reactivity with the bone tissue increasing the anchorage of the bio-ceramic film with the biological tissue.

Also the angles of deposition (with respect to the target-normal direction) and substrate temperature are critical in determining the relative amount of ablated material, deposited thin film, and the morphology of the deposited film \[77\].

The Pulsed Laser Deposition (PLD) technique has been employed also to deposit a diamond-like carbon (DLC) film on different substrates of biomedical interest (Ti, Ti-alloys, SiO\(_2\) and AISI 316L). Results indicate that at little deposition angles, below 15°, the structure of the carbon crystals is well defined and rich of sp\(^2\) and sp\(^3\) chemical bonds with respect to the glassy carbon target. At large deposition angles, higher than 15°, the films contain only amorphous phases showing also here as the angle of deposition is a critical parameter.
The future of the investigation of the carbon plasma is in the direction of laser ion source (LIS), ion implantation, hadrontherapy, and carbon nanostructure generation. The ion implantation technique now can use the implant of multi-energetic carbon ions produced by laser-generated plasma in order to modify the chemical and physical properties of different surfaces. In the medical field, the hadrontherapy requires carbon ion beams accelerated at 4700 MeV to irradiate tumours. In microelectronics and biochemistry are requiring instrumentation to generate carbon nanostructure aggregates and films for different aims [72].

Another investigation of this work regards the capability to induce modification in different polymeric materials by energetic pulsed lasers. Targets as a pure UHMWPE sheets and UHMWPE/CNT nano-composites with carbon nano-tube (CNT) weight content between 0.5% and 1.0% have been investigated. Modification concerned only the superficial region of the irradiated polymer, up to a depth of about 160-200 µm. Results indicate that the polymer hardness, the wet ability, and the electrical resistance values change with irradiation time and the nano-tube content in the polymer.

The development of new laser sources, advanced laser optics and electronic control systems offer new opportunities for lasers, particularly in modifying surfaces of many hydrogenated polymers [113].

Finally, laser ion sources (LIS) was employed to realize a new type of implanter called Laser Ion Implanter (LII). This implanter permits a multi-energetic ion implants (with ions energy ranging from 10 keV to 400 keV) on a given substrate surface to improve the physical and chemical properties. The ion trajectories from target source to substrate were simulated by using the computer program TOSCA (OPERA 3D). These simulations have shown that the insertion of a magnetic field of 2 Tesla improves the ion focalization along the system axis increasing the
implanted dose per laser pulse. While, in order to accelerate the ions towards the substrate, the target source was positively polarized (+50 keV). With SRIM simulation, we have the final Ti depth profile due to the convolution of different ion energy deposition demonstrating that ions are implanted in the substrate in uniform way and up to depth of 340 nm.

The computer simulations represent a preliminary tentative to fix some parameters of a simple and compact implanter accelerator. It find important applications in the field of ion implantation of metals, semiconductors, ceramics and polymers’ surfaces, which can be chemically and physically modified by high ion dose implantation. Today the ion implantation has achieved a wide application in the semiconductor industry because of the possibility to alter the conductivity of the material of several orders of magnitude by introducing small quantities of dopant atoms; for the ability to control the number of implanted dopants; and the possibility to place them at the desired depth.

This thesis work has brought to the publication of 8 works on international reviews with referee, 6 participations at international congresses, 6 participations at national congresses, and 4 activity reports.
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