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New trends in femtosecond Pulsed Laser Deposition
and femtosecond produced plasma diagnostics

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ABSTRACT

The availability of compact table top amplified femtosecond lasers and the technical simplicity of experimental
design have opened the way to many recent and fast developments towards thin film elaboration by Pulsed Laser
Deposition (PLD) with ultra short laser pulses, with the aim of producing materials of high quality previously
unattainable or attainable only through more complex means.

The first developments of PLD using femtosecond lasers were made on Diamond-Like Carbon thin films elaboration,
with the attempt to reach high $sp^3$ content. PLD with ultra short pulses was used recently to deposit several systems
such as quasicrystals or oxides with a transfer of the target composition to the deposited films, even for compounds with
complex stoichiometry. Femtosecond laser ablation from solid targets has shown its capability in producing
nanoparticles of different materials, even in high vacuum conditions. Nanostructured films of doped Diamond-Like
Carbon were obtained recently, opening the way to large applications towards functional materials.

The characteristics of the plasma are a well-suited signature of the physics of laser-matter interaction and plasma plume
creation and expansion. Recent studies on the control of the film growth and femtosecond PLD processes will be
reported.

Emphasis on actual capability of the existing sources to elaborate high quality materials will be questioned in terms of
energy per pulse, time width, repetition rates but also in the need for further source development and beam shaping
improvement.

Keywords: Pulsed Laser Deposition, Femtosecond laser, Diamond-Like Carbon, Nanoparticles

1 INTRODUCTION

Pulsed laser deposition (PLD) has been proved to be an effective technique for the deposition, at low
temperature, of a wide variety of thin film materials\(^1\). A large range of materials is concerned, such as oxides,
nanostructured materials or hard and wear resistant diamond-like carbon (DLC) coatings, for example. The energetic
characteristics of the plasma produced by laser ablation play an important role in the synthesis of thermodynamically
metastable materials, such as diamond-like carbon\(^2\). PLD allows a precise control of the concentration of elements
impinging upon the growing films, and this is of particular interest to deposit doped and alloyed films in a controlled
and reproducible way, compared to other deposition techniques. Femtosecond lasers challenge excimer lasers for high
quality thin film preparation and high-precision micromachining. The pulse duration makes possible to achieve higher
spatial resolution but also higher laser intensity than nanosecond lasers. The use of femtosecond lasers in PLD
originates from the possibility to deposit particulates-free films, compared to nanosecond PLD, as already investigated
for DLC\(^3\). The capability to deposit metastable materials, such as DLC or cubic phases of nitrides, and the possible
congruent ablation for complex stoichiometry has increased the interest in femtosecond PLD as an alternative
interesting deposition technique. Ultrashort laser pulses can significantly reduce the extent of heat conduction into the
target, leading the irradiated material in extreme conditions of temperature and pressure\(^4,5\). The subsequent relaxation of
the heated material results in the ablation of the target surface with expulsion of matter form of atoms and ions, as well
as clusters and nanoparticles\(^6\). In the case of femtosecond laser ablation, the kinetic energy of the fastest ejected species
can be increased up to a few keV\(^7\) leading to a better adhesion of the film on various substrates\(^7\).

Femtosecond laser ablation is used from 1999 to deposit successfully various kinds of films, in particular pure
DLC films\(^3,7,8\). These films exhibit $sp^3$ content in the range 40–75%, with interesting mechanical properties, low
friction and high wear resistance. Pulsed laser ablation with ultrashort laser pulses has been also recently demonstrated as an interesting technique for the generation of nanoparticles of different materials\textsuperscript{13-16}. In particular, it has been already demonstrated\textsuperscript{14,15} that femtosecond laser ablation is able to produce films of metallic and non-metallic materials formed by nanometric particles.

Diamond-like carbon coatings, with high sp\textsuperscript{3} content, present a lot of interesting properties using for practical or potential applications\textsuperscript{17}. They are characterized by high wear resistance, low friction coefficients, chemical inactivity and high corrosion resistance. These properties make the films good candidates as biocompatible coating for biomedical devices and tools. Various medical devices – including hip and knee joints, coronary stents, heart valves, intraocular lenses – are implanted in the human body to fulfill biological and mechanical functions. The use of DLC films as protective films for such purposes was already suggested in the early 1990s\textsuperscript{18}.

In this work, we carried out various materials deposition by femtosecond PLD, extending from DLC, to metallic nanoparticles and composite films, corresponding to DLC films doped with nanoparticles of metals.

We will present, in a first part, adherent DLC coatings as protective films on a 22.2 mm in diameter hemispherical femoral head of hip joint prosthesis in order to improve its wear life and lifetime. The adhesion of DLC films has been enhanced without using underlayers, which may be forbidden due to biological reactions with the surrounding tissues.

We have also investigated the deposition of metallic (copper, aluminium, tantalum, nickel) nanoparticles by femtosecond PLD. The morphological and structural characterizations will be presented in a second part of this paper.

Finally, in a third part, the present work will belong to the attempts to deposit doped diamond like carbon films by femtosecond PLD. The films have been investigated by coupling several techniques, including X-ray photoelectron spectroscopy (XPS), grazing incident angle X-ray diffraction (GIXRD), high resolution scanning and transmission electron microscopies (SEM, HRTEM). Some of us have already deposited a-C: Ni and a-C: Ta, leading to a distribution of metallic Ni or Ta clusters embedded in the carbon network\textsuperscript{19,20}. In the present work, we will examine more accurately the deposition of tantalum-doped DLC. We will present a tentative correlation between the films properties, by the examination of the crystalline structure and the formation of a thin layer of tantalum carbide; and the plasma plume properties, in terms of temperature of the tantalum nanoparticles and the kinetic energy of the impinging species on the substrate.

## 2 DIAMOND LIKE CARBON DEPOSITION

The experimental arrangement used in our work has been detailed elsewhere\textsuperscript{7,11}. Diamond-Like Carbon thin films have been deposited onto various substrates (silicon, UHMWPE, stainless steel) at room temperature, by ablating high purity graphite target (99.997 %). The femtosecond (10\textsuperscript{-15}s range) laser (Concerto, BMI/TCL) working at 800 nm, with an output energy per pulse of 1.5 mJ and a pulse duration of 150 fs at a repetition rate of 1 kHz, is focused with an incidence angle of 45° onto the target by a 40 cm focal length lens. The pulse duration is estimated to be 150 fs by autocorrelation measurements. The laser beam is introduced into the chamber through a 3 mm thick quartz window and the substrate is located in front of the target surface at a distance of about 4 cm. Experiments take place in a high vacuum chamber (residual pressure below 5.10\textsuperscript{-8} mbar). Before the deposition, the substrates have been ultrasonically cleaned for 3 minutes in acetone and ethanol bath before been loaded into the deposition chamber. During the deposition processes, different intensity levels have been achieved by varying the focusing of the laser spot.

In biomedical applications such as joint prosthesis, coating adhesion is paramount. Whatever the deposition process, DLC films on 316L stainless steel substrates generally show weak adhesion\textsuperscript{17,18}. In order to improve this property, \textit{in situ} sputter cleaning of the substrates has been carried out before DLC deposition. The cleaning process consists in removing the contaminated and oxidized surface layers by the argon plasma phase prior the DLC deposition (\textbf{Figure 1a}). The thickness of the etched layer and the substrate roughness after etching, R\textsubscript{s}, have been measured by profilometry; they were found to be respectively 0.01 Å and 20 nm. The substrate roughness is not significantly modified by etching. The adhesion of DLC films have been measured by tensile tests\textsuperscript{12} and the effect of etching has been quantify (\textbf{Figure 1b}). On non-etched substrates, DLC films exhibit poor adhesion. The film deposited at a fluence of 1.3 J cm\textsuperscript{-2} shows no adhesion at all and at higher fluences, respectively 2.8 and 4.2 J cm\textsuperscript{-2}, adhesion is about 20 and 30 MPa only. When etching is performed, adhesion is dramatically enhanced: whatever the fluence, cohesive ruptures in glue instead of adhesive ruptures between the DLC film and the substrate are observed, thus adhesion values of DLC...
films are estimated to be higher than 45 MPa. These results are in agreement with those published by Morshed et al.\textsuperscript{21,25} showing that sputter cleaning prior deposition significantly enhances the film adhesion.

![Image](image1.png)

Figure 1: Enhancement of the adhesion of DLC films on metallic substrates:
(a) sputter cleaning of the femoral head of a hip joint prosthesis under argon plasma
(b) adhesion of coatings on stainless steel substrates determined by tensile tests

From previous works\textsuperscript{7}, where we examined the possibility to deposit homogeneous DLC films on larger surfaces than the conventional cm\textsuperscript{2} area of deposition used for most of PLD devices, homogeneous DLC films can be deposited onto a 22.2 mm diameter hemispherical surface of a 316L stainless femoral head. The femoral head is sputter cleaned in an argon atmosphere prior to carbon deposition by using the procedure detailed previously. Then DLC has been deposited during 30 min at a laser fluence of 2.8 J cm\textsuperscript{-2}. This time of deposition has been optimised to achieve the same order of magnitude of film thickness (about 150 nm) than on conventional cm\textsuperscript{2} surfaces, taking into account the rotation of the femoral head during deposition, with a tilt of 45° in respect to the direction of plasma expansion\textsuperscript{7}. The uncoated and DLC coated femoral head are depicted in Figure 2.

![Image](image2.png)

Figure 2: Uncoated (A) and DLC-coated (B) femoral head in AISI 316L stainless steel\textsuperscript{12}

3 SYNTHESIS OF NANOPARTICLES

Pulsed laser ablation with ultrashort laser pulses has been recently demonstrated as an interesting technique for the generation of nanoparticles of different materials\textsuperscript{13-16}. In particular, it has been already demonstrated\textsuperscript{14,15} that femtosecond laser ablation is able to produce films of metallic and non-metallic materials formed by nanometric particles. The plasma plume created under conditions of clusters formation has been studied mainly by Time Of Flight measurements, spectroscopic characterization or imaging of the plasma plume. The presence of three components in the kinetic energies of the ejected species has been observed by various authors and for different materials\textsuperscript{6,14-16,26-28}. The
first component appears to correspond to fast ionic species, whereas the second one correspond to neutrals or ions. A later component, resting closer to the target till very long time delays after the laser pulse and expanding with a slow energy is attributed to nanoparticles. The mechanisms of formation of these nanoparticles have been investigated by Molecular Dynamics simulation\textsuperscript{5,28}. The nanoparticles are directly ejected from the target, due to phase explosion and the presence of overheated liquid in the irradiated materials. When working at low laser fluence close to the ablation threshold\textsuperscript{5}, the mechanical spallation can be at the origin of the ejection of cold and large chunks. However, from molecular dynamics simulations, the presence of the nanoparticles may not be attributed to condensation processes during the plume expansion, as it is the case in nanosecond ablation.

We have investigated the deposition of metallic (copper, aluminium, tantalum, nickel) nanoparticles by femtosecond pulsed laser ablation. The experimental arrangement is the same as the one used for the deposition of Diamond-Like Carbon thin films. The femtosecond laser is focused with an incidence angle of 45° onto the metallic target copper, aluminium, tantalum, nickel. Experiments take place in a high vacuum chamber (residual pressure below 5.10^{-8} mbar) under vacuum or residual pressure (inert gas or reactive gas). Before the deposition, the substrates have been ultrasonically cleaned for 3 minutes in acetone and ethanol bath before been loaded into the deposition chamber. During the deposition processes, a constant laser fluence value of 2.8 J/cm\textsuperscript{2} has been used. The morphology of the clusters has been examined by high resolution scanning electron microscopy (FEG-SEM). The films exhibit nanostructures containing metallic clusters in the range of about 100 nm as reported in Figure 3.

In order to go further in the investigation of the crystalline structure, the films constituted by the stacking of nanoparticles were analysed by Grazing Incidence X-Ray Diffraction (GIXRD). The spectra were obtained with an incident X-ray beam angle of 0.7°. The full width at half maximum (FWHM) of the crystalline phases identified from the spectra are consistent with nodule sizes in the range of 100 nm. This crystallites size is about the same order of magnitude than the morphological size. The grain size of the clusters deposited under residual pressure appear to be greater than the grain size of the clusters deposited under vacuum. This general increase with the ambient pressure may appear quite surprising if the nanoparticles are emitted directly from the target by phase explosion mechanisms. The lattice parameter of the clusters has been determined from GIXRD investigations. In some cases, the lattice parameter of the clusters appears to be slightly different from the lattice parameter of bulk materials. As an example, the lattice parameter of the aluminum clusters is smaller than the lattice parameter of the bulk materials. We can attribute this observation to a compression stress in the cluster. These compressive stresses are frequently observed in films elaborated by Pulsed Laser Deposition. The introduction of compressive stresses in the aluminum nanoparticles was also observed by Eliezer et al\textsuperscript{13}.

![Figure 3: Synthesis of nanoparticles by femtosecond pulsed laser deposition:](image)

(a) aluminium nanoparticles (b) tantalum nanoparticles
4 DEPOSITION OF COMPOSITE FILMS AND CORRELATION WITH PLASMA PLUME PROPERTIES

We have synthesized metal containing DLC films (a-C:Me) by ablating respectively a target of pure graphite (purity 99.997%) and a target of pure metallic target (tantalum or nickel, purity 99.9%). The principle of this co-deposition consists to focus alternatively, by using a shutter, the femtosecond laser (Concerto, BMI/TCL, k =800 nm, pulse duration 150 fs, repetition rate 1 kHz, energy per pulse 1.5 mJ) onto the graphite’s target, and thus onto the tantalum’s target. The irradiation times on each target have been selected to achieve the desired stoechiometry, taking into account the deposition rate of each element determined in a preliminary set of experiments. This sequence of ablation is repeated during a certain number of runs depending on the thickness required for the coatings. Typically 240 runs of 1s with metal crossed with 241 runs of 9s with carbon lead to films in the micrometer range. The last ablated species is systematically carbon. The films were grown at room temperature in a deposition chamber evacuated to a base pressure of $10^{-5}$ Pa. The laser has been focused with an incident angle of 45° on the targets, with an energy density of 2.6 J/cm². More details on this deposition procedure have been published in previous papers.

The spatio-temporal behavior of the plasma plume created by the ablation of the graphite target and the metallic target has been investigated by using a fast shuttered intensified CCD camera (5ns exposure time). The electronic device is synchronized with the laser pulse with reduction of the repetition rate of the femtosecond laser. This spatially and temporally resolved imaging of the laser-induced plasma plume has been completed by temporally resolved emission spectroscopy. These measurements allow us to access to the nature of the emitting species and the kinetic energy of the particles, which is correlated to the quality of the films.

SEM observations of the a-C-Ta film (Figure 4a) show evidence of the nanostructure of the film surface. These features, analysed by the imaging system, allow quantification of the size distribution of clusters present in the film (Figure 4b). A wide size distribution is observed between 15 nm and 175 nm. The average size is 82 nm with a standard deviation of 49 nm. Specimens have been also examined by EELS, confirming, through a transmission view, the nanostructure of the film. A zero-loss image of a 100 nm thick coating highlights the morphology of the films, consisting of dark metallic nodules (100 nm or less) dispersed in a brighter matrix. A more detailed investigation of the a-C:Ta film has been achieved by HRTEM.

![Figure 4: Synthesis of doped Diamond-Like Carbon films](image)

(a) FEG-SEM image of tantalum-doped diamond-like carbon film (b) size distribution of the clusters embedded in the film.
In order to go further in the investigation of the crystalline structure, the a-C:Ta film (100 nm thick) has been analyzed by GIXRD (Grazing Incidence X-ray Diffraction). The spectrum (Figure 5a) has been obtained with an incident X-ray beam angle of 0.7°. We identify three main contributions corresponding to the different phases present in the film:

– a centered cubic tantalum phase ($\alpha$-Ta) which is the stable phase in normal pressure and temperature conditions. The tantalum target used for deposition is $\alpha$-Ta.

– a metastable phase, corresponding to metallic tetragonal tantalum ($\beta$-Ta), which has been already observed at high temperatures (>800 °C)\(^{29}\).

– probably an amorphous phase whose signal corresponds to the bump centered on the most intense peak of the stable phase ($2\theta=38^\circ$).

From the combination of the previous investigations, we have observed that the present a-C:Ta film (15 at.% Ta) consists in three kinds of metallic nodules with diameters in the 10–100 nm range. Indeed, femtosecond PLD leads to nanostructured films with grain size in the nanometer scale and properties significantly different from nanosecond PLD films\(^{30,31}\). As already pointed out, the nanostructure seems to originate from the drastic effects of femtosecond laser–matter interaction, as phase explosion\(^{32}\) or explosive melting\(^{33}\). Moreover, mass spectrometry analyses of the plasma plume\(^{34}\) shows the presence of clusters in the plume, which can be correlated to the nanostructure of the films. As the deposition technique is a non-equilibrium one, we have obtained in the present work two crystalline phases ($\alpha$-Ta and the metastable $\beta$-Ta), compared to the only one present in the target ($\alpha$-Ta). The metastable phase is present at high temperatures (higher than 800 °C), leading to the conclusion that species in the plasma plume induced by femtosecond ablation reached temperatures higher than 800 °C. The carbonaceous structure in the tantalum alloyed DLC appears to be quite similar to the carbonaceous structure related to pure DLC films deposited by the same femtosecond PLD process\(^{26}\). The nature of the species present in the plasma plume during the femtosecond laser ablation of the metal target has been investigated by spectroscopic emission measurements.

As an example, the spectrum recorded at a delay of 1 µs after the ablation by a femtosecond laser of a pure tantalum target is reported on Figure 5b. The emission is characterized by a continuum spectrum which is attributed to the slower component of the plume, i.e. hot nanoparticles\(^{27}\). This continuum spectrum can be compared to black-body emission spectrum. We deduced from these measurements the nanoparticles' temperature of about 4000 K. This temperature is much higher than the required temperature for the formation of the metallic tetragonal tantalum ($\beta$-Ta), 800 °C. We can then conclude that tantalum nanoparticles may have suffer an allotropic transformation during their trip in the plasma plume towards the substrate.

Figure 5: Deposition of metal doped Diamond-Like Carbon films

(a) Grazing angle X-ray diffraction spectra of the a-C:Ta and a-C:Ti films, observed with an incident X-ray beam angle of 0.7°. The un-indexed peaks correspond to the doped-Si substrate.

(b) Emission spectroscopy spectrum of the tantalum plasma created under femtosecond ablation of a pure tantalum target.
By HRTEM investigations\textsuperscript{20}, the external part of most nodules seems to contain a higher amount of carbon. This may be attributed to the well known chemical affinity between tantalum and carbon through the formation of carbides. Since GIXRD investigations do not identify any tantalum carbide phase, probably such a carbide, if it exists, is so thin and/or so imperfectly crystallized, that the diffraction technique is unable to identify it. One way to go further is to perform XPS in order to investigate the top surface of the film, which is consisted of a thin carbon layer (in agreement with the deposition procedure) covering the tantalum nodules. XPS measurements have been reported elsewhere\textsuperscript{20}. Carbon, tantalum and a low quantity of oxygen (less than 2\%) are detected by XPS in the C:Ta film. The spectrum of the film shows an asymmetric C1s signal broader (FWHM= 2 eV) than those related to diamond and graphite (FWHM=1 eV). From the curve fit analysis of this C1s signal in four Gaussian contributions, two different binding energy components, respectively, at 283.9 eV and 283.5 eV, may be attributed to the tantalum–carbon bond in TaC carbides\textsuperscript{35}. The affinity of tantalum with carbon is confirmed with the Ta 4f feature, where the Ta 4f\textsubscript{7/2} and 4f\textsubscript{5/2} peaks are located respectively at 23.1 eV and 24.9 eV. From the literature the peak 4f\textsubscript{7/2} is located at 21.5 eV, 22.9 eV and 26.6 eV, respectively, for metallic tantalum\textsuperscript{36}, tantalum carbide\textsuperscript{35} and tantalum oxide\textsuperscript{37}.

Taking into account the energy resolution of our spectrometer and the experimental position of the Ta4f\textsubscript{7/2} peak in the present work, we can conclude that the thin top surface layer probed by XPS is mainly constituted by tantalum carbide. No attempt to quantify the stoichiometry of the carbide has been performed, since such an approach requires a specific deep XPS investigations\textsuperscript{38}. The formation of the thin top layer of tantalum carbide during the deposition require obviously a good chemical affinity of tantalum with carbon, but also a high energy of the carbon species impinging on the growing tantalum film. Spectroscopic measurements of the carbon species during the femtosecond ablation of the graphite target have been carried out. As an example, the emission spectroscopy spectrum of the carbon plume recorded at a delay of 500 ns after the femtosecond laser ablation of the graphite target is reported on Figure 6. From the identification of the spectral lines\textsuperscript{39}, one can conclude to the presence of both atoms and ions in the plume. The kinetic energies of these species have been determined by Time of Flight measurements. We obtained a mean kinetic energy of carbon ions of 250 eV. The penetration depth of carbon ions impinging on a tantalum surface with an energy of 250 eV can be estimated by a Monte Carlo simulation (TRIM code)\textsuperscript{40}. This program calculates the energy loss, the range of action or the target damage due to ions bombardment of a surface. The range of action of the high energy carbon ions is about 2nm, which is of the same order of magnitude than the thickness of the thin top layer probed by XPS. Due to the well-known chemical affinity between carbon and tantalum, the interface between the tantalum clusters and the carbonaceous matrix may be, as revealed by XPS, a tantalum carbide phase.

Figure 6: Emission spectroscopy spectrum of the carbon plasma created under femtosecond laser ablation of a pure graphite target
5 CONCLUSION

The present work concerns pulsed laser deposition using femtosecond lasers. Various materials have been synthesized by femtosecond PLD, including Diamond-Like Carbon thin films, nanoparticles of metals and composites materials corresponding to metal-doped Diamond-Like Carbon. Fast imaging of the plasma plume and emission spectroscopy measurements have been achieved in order to correlate the properties of the films with the main features of the plasma plume, as the nature and the energy of the deposited species.

The deposition of DLC thin films on non-conventional (larger than the conventional cm² and hemispherical) substrates has been investigated by femtosecond pulsed laser deposition on various substrates, including AISI 316L steel used in hip joint prostheses. Films are predominantly sp³ and improvement of the adhesion, by almost 100% on AISI 316L steel substrates, has been performed by sputter cleaning of stainless steel substrates prior to deposition. These results combined to low wear coefficients, in the $10^{-8}$ to $10^{-7}$ range, show that DLC thin films deposited by femtosecond PLD are good candidates as protective coatings for articular joints.

The deposition of nanostructured coatings of tantalum-doped diamond-like carbon (a-C:Ta) by femtosecond PLD has been investigated. The alternative ablation of a tantalum and a graphite target leads to nanostructured coatings consisting in nanoparticles of tantalum embedded in an amorphous matrix of Diamond-Like Carbon. The size distribution of the tantalum nanoparticles has been examined by FEG-SEM. The cristallinity of these nanoparticles has been investigated by Grazing angle X-Ray Diffraction. The crystallinity of these nanoparticles has been examined by FEG-SEM. The cristallinity of these nanoparticles has been examined by FEG-SEM. The cristallinity of these nanoparticles has been examined by FEG-SEM.

A possible way to achieve higher quality of the films would be to control and design the laser pulse, as by a temporal shaping, in order to produce the required species or kinetic energy of the species necessary to a particular phase growth.

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