Characterization of thin films for TNSA laser irradiation

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Abstract. Thin films of hydrogenated materials have been prepared, at Messina University, to be irradiated by high intensity lasers in TNSA conditions in order to accelerate high energetic protons with high yield and directivity. Film composition was based on polymers, metals, multilayers and nanostructures embedded in polymers. The preparation methods were different and based on different deposition techniques. High vacuum condition, nanostructures, carbon nanotubes, metal oxides and hydrates, were employed. Targets were prepared as a sheath with thicknesses ranging between 0.1 and 100 \( \mu \)m and surfaces of the order of some cm\(^2\). Targets were characterized in terms of thickness, roughness, surface morphology, colours and absorption coefficient in the wavelength range 250 nm-1300 nm. Peculiar attention is given to samples with high absorption coefficient in order to improve the energy transfer from the coherent light to the generated plasma.

1. Introduction
In 1982 at Los Alamos National Laboratory have been achieved protons of 0.5MeV by using a laser at \( 10^{15} \) W/cm\(^2\) of intensity. In the last 30 years, occurred improvement on the geometry and composition of targets, on the focalization of \( fs \) lasers, more knowledge on the parameters of laser-generated plasma, development of detectors with high reliability, faster, more resistant at high temperature and low background current. The state of art in 2001 evaluates the dependence of many parameters (temperature, density, electric fields, ion charge state distributions,…) on the product \( I\lambda \), where I is the laser intensity and \( \lambda \) its wavelength, and shows that the ion acceleration increases with such parameter [1]. Intense charge separation in plasma and high electric fields, of the order of TV/m, has been generated inducing ions acceleration by high energy and short laser pulses [2]. Many laboratories in the world are accelerating protons up to 40 MeV/nucleon, using the TNSA (Target Normal Sheath Acceleration) approach. Recently, research has increased significantly in the direction of replacing conventional accelerators for the production and acceleration of ion beams to demonstrate the clinical applicability of laser driven-proton by irradiation of solid targets with laser pulses at high intensities. With the aim to fully utilize the advantages of protons beams laser-generated for applications, from bio-medicine to nuclear physics and from microelectronics to chemistry, the process of production of protons can be optimized using suitable hydrogenated targets. It is well-known that when an electromagnetic wave impinges a solid target, part of the radiation is adsorbed, part is scattered, part is transmitted and part is reflected. Actually, the main objective is the maximization of the absorption efficiency of the matter in order to enhance the laser energy transmitted to the target and consequently

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the transfer of energy to the plasma in order to increase its temperature, density and electric field driving ion acceleration. The amount of charged particles emitted during the laser-matter interaction depends on the intensity of the absorbed radiation. In order to evaluate the amount of energy released to a solid target during the laser-matter interaction it is important to investigate on the reflectivity and absorption coefficient of the irradiated targets. The practical applications have been focused on the techniques to produce thin films to be irradiated in TNSA conditions and porous and nanostructured samples to increase the absorption effects. Thus the investigation of their optical properties becomes an important objective of the research [3]. Samples containing nanostructures, hydrogenated targets, multilayer films and microporoues targets, are able to increase the kinetic energy of the accelerated species by the non–equilibrium processes developed in laser irradiation of TNSA foils [4].

2. Materials and methods
With the aim to arrange targets with peculiar properties such as low reflectivity, high porosity and roughness of the surface, low thickness, and high absorbent nanostructures embedded, different thin film deposition techniques have been employed. In this work we will discuss only four of them that modify physical characteristics of thin films, such as the surface morphology and the inclusion of micrometric and nanometric particles. A brief description of the used four methods for thin film preparation is described in the following.

2.1. Pulse Laser Deposition (PLD)
PLD of Ti, Au, Cu and Pd thin films were obtained irradiating metallic bulk targets by laser at 0° incidence angle and positioning the substrates at different distances from the target. Substrates were polymers (mylar and polyethylene). The bulk metals were fixed on a rotating carrousel to allow a fresh surface ablation in high vacuum (10^{-6} mbar). A Nd:YAG laser at the fundamental wavelength (1064 nm), 300 mJ pulse energy, 9 ns pulse duration, 10 Hz repetition rate was used [5]. Generally Cu, Au, Pd, Ti particles have been deposited on 0.9 μm thickness mylar (C_{10}H_{8}O_{4}n) or polyethylene (CH_{2}n).
Inside the vacuum chamber the angles in which have been fixed the substrates were 15°, 20° and 45° with respect to the normal target direction and distances ranging between 8.5 cm and 16 cm with respect to the target. Film thicknesses between 100 nm and 10 μm were obtained.

2.2. Ion Sputtering
Ion sputtering has been performed by using 1-3 keV Ar^+ ion gun with a ion current flux of 10-50 μA incident at 45° on metallic targets (Cu, Ag, Au) and on polymeric target (PMMA). Sputtered metallic atoms were deposited on polymeric substrates (mylar and polyethylene), from 0.6 to 6 μm thickness. The ion irradiated surface was 1 cm² and the Ar incident doses were from about 10^{15} up to about 10^{17}/cm². The low ion energy induces bombardment in nuclear stopping power regime and the structural damage modifies the morphology of the target [6]. Stopping and Range of Ion in Matter (SRIM) code was employed to predict the behaviour of 2 keV Ar^+ ions interacting with the matter and to evaluate the sputtering yield (number of emitted atoms per incident ion). As for PLD, the thickness of deposited thin films has been measured using 5 MeV energy loss of alpha particles emitted form a collimated Am^{241} radioactive source. The transmitted alpha particles though the prepared thin film were detected with and without the deposited thin film. On mylar, thin films of Cu, Ag and Au with thicknesses ranging between 10 nm and 500 nm were prepared. Object of the laser TNSA investigations were both the mylar covered by thin metallic films and the same sputtered metallic targets, 10-50 micron in thickness, which show grain contours enlargement produced by the sputtering effect, as SEM image investigations have demonstrated.

2.3. Spin coating
Spin coating involves accurately dispensing a liquid onto a substrate then spinning to achieve a uniform defect-free film. It employs the use of extremely precise rotation control coupled with a closed, fully optimized process chamber. A typical spin process consists in three steps:
1) The liquid drop is deposited on (or near) the centre of the circular rotating substrate (silicon wafer or glass), generally 5cc volume of the resin fluid is employed.

2) The combination of spin speed and time selected will determine the final film thickness. This step takes some seconds and depends on the solution viscosity and temperature.

3) The time and the air permit to regulate the dry time to obtain a solidified thin film on the substrate. Finally the thin film is detached from the substrate. In our laboratory thin film deposition was performed by using carbon nano-structures embedded in an acrylic resin in which ethanol has been added in order to reduce the viscosity. C-structures have had a size range between 10 and 100 nm which are dispersed in solution and left in a ultrasonic bath for 1 hour. 5cc volume of the resin fluid was employed. The solutions concentration was obtained using micrograms of C-powder containing carbon nanoparticles in 4 ml of resin. A 1100 rmp was the spin speed employed for 480 seconds time spinning.

2.4. Thermal Sintering

It is a technique able to embed in a matrix of Ultra High Molecular Weight Polyethylene (UHMWPE), 3x10^6 g/mol molecular weight, 99.7% purity, 50% crystalline and 50% amorphous, micrometric and nanometric fillers, such as Fe_2O_3, C_{16}H_{18}N_3SCl, carbon nanotubes (CNT) and carbon nanoparticles. The fillers with a main size ranged between 50 nm and 100 nm and with a concentration ranged between 0.01 wt% , and 10 wt%, colour the polymer red for iron oxide, blue for methylene-blus and black for carbon. The procedure to realize thin targets consists in the use of ethanol mixed with carbon nanotubes in concentrations of 0.01%, 0.5%, 1%, 2% in order to facilitate their dispersion and avoid the mechanical cracking of composed final polymeric film. The powder of polyethylene at ultrahigh molecular weight was put in a mould, to form a flat and circular sample which thickness was from 10 to 100 μm and diameter of 10 mm. The mould was positioned inside the hydraulic presser at a final temperature of 200°C and at a final pressure of 200 bar for a time of 20 minutes. Final thicknesses were measured with surface profiler and/or mechanical micrometer.

2.5. Optical characterizations

The thin films prepared by the different techniques, having different compositions, thickness and geometry, were arranged in a target holder to perform their successive optical characterization. A Hg-Ar lamp, with characteristic lines at wavelength ranging between 200 and 1200 nm, was used as multi-monochromatic radiation source. The Fig. 1 shows the spectrum obtained by using the above-mentioned lamp that contains argon and mercury gas. It indicates the characteristic lines in UV, Visible and IR regions, and the relative intensity used for absorption measurements as a function of the wavelength. The incident radiation impinges the samples fixed into the holder-target with a normal incidence. The transmitted light from the sample is connected by an optical fibre and it is sent to a Horiba Jobin Yvon Spectrograph. The absorption coefficient of the sample was evaluated by using the Beer-Lambert’s law [7]:

\[
\mu = \left( \frac{1}{x} \right) \ln \left( \frac{I_0}{I} \right)
\]

where the absorbance \(\mu\) of electromagnetic wave, is given in terms of incident light \(I_0\), transmitted light \(I\) and thickness \(x\) of the used sample used. The experimental set-up consists of a Lynear spectroscopy software, that acquires 160 spectra per second that are stored and averaged on a PC, a suitable target holder for the lamp, the sample and the fibre and a PC for data elaboration and for the power supply of the lamp. The sample thickness was measured using the energy loss of alpha particles.
(coming from a radioactive source of Am-241) or the surface profiler with indeterminacy of the order of 10 nm (Tencor P-10).

![Figure 1. Hg-Ar lamp spectrum.](image)

### 3. Results

The plot in Fig. 2 shows the transmission measured in a sample prepared by PLD technique depositing 52 nm of Pd on a mylar substrate 0.9 μm thickness. The points in the plot correspond to the values of the used wavelength lines. The sample, in the visible region 400 nm-700 nm, has a transparency comparable with the pristine ones. While in the infrared region, for wavelengths higher than 700 nm, it shows a higher absorption of the order of 40%. Also absorptions bands are present in the near UV region that reaches about 40% at 300 nm radiation.

![Figure 2. Transmission measurements vs. wavelengths for mylar and Pd/mylar thin film.](image)

Polymethylmetacrylate (PMMA) targets, \((C_5O_2H_8)_n\), have been sputtered by 2.5 keV Ar ions in order to induce micrometric widening of the grain contours in the polymer surface. The evaluations of argon ions distribution in PMMA were achieved by using SRIM code [8] at the same conditions of the
experimental setup. The sputtering yield of C, O and H atoms at an incidence angle of 45° is 36.44, 15.52 and 12.4 atoms/ion for C, O and H, respectively. The argon ion distribution reaches 80 Å range penetration inside the PMMA in which each ion argon removes up to 36 carbon ions producing collision, vacancies, defects and disorder in the polymer. Thus the polymer modification is extremely superficial. The samples have been treated at the same experimental conditions in order to provide ion doses at $10^{15} \text{/cm}^2$, $10^{16} \text{/cm}^2$ and $10^{17} \text{/cm}^2$. Optical investigations performed on these modified targets show an increase of the absorbance with the increase of employed doses. Fig. 3a shows a comparison between the absorbance for pristine PMMA and PMMA samples treated with a high Ar$^+$ absorbed dose. For the higher doses, measurements indicate a lower absorption in the UV region range and a significant increment up to 40-50% of the absorption coefficient in the IR range, above 800 nm, occurs.

![Absorbance vs. wavelength](image)

**Figure 3.** Absorbance vs. wavelength, for pristine and PMMA at different sputtering doses (a), and optical transmission vs. wavelength, for resin containing and not TiH$_2$ nanostructures (b).

Fig. 3b shows the optical transmission relating resin pristine and resin containing TiH$_2$ nanostructures, 50-100 nm sized, embedded by using the spinning deposition technique. This last target, has an interesting behaviour at the UV wavelength and at the IR region due to the influence of metallic component in the composite, instead in the VIS region, it presents a transmission of the order of 85% - 90% very close to the pristine sample.

The targets prepared by thermal sintering, investigated at wavelength between 250 nm and 1000 nm, show different absorption coefficients in the UV, VIS and IR regions as a function of the kind, of the thickness and of the concentration of nanoparticles embedded in the polymeric matrix. Fig.4 reports the results of absorbance vs. wavelength measurements obtained for 100 μm thickness pure polyethylene films and for polyethylene containing different nanostructures. It can be observed as carbon nanotubes (CNT) and nanoparticles embedded into polyethylene (PE) at 0.5%-1% in weight concentration, show higher absorbance with respect to the pristine polymer of polymer containing other nanostructure species (methylene blu) in similar concentrations.

4. Discussion and conclusions

From the comparison between the absorption coefficients measured for different polymeric thin films it is possible to observe that high absorptions are obtained in the IR region for mylar films covered by thin metal films, such as Pd, Ti, Au and Cu (see Fig. 2), or for high Ar$^+$ ion doses sputtered PMMA (see Fig. 3.a), or for polyethylene in which peculiar nanostructures, such as carbon nanotubes and carbon nanoparticles, are embedded to concentrations of the order of 1% (see Fig. 4).

The samples prepared by spinner, show the best absorption in the IR region inserting in the solution TiH$_2$ nanostructures (see Fig. 3.b).
Thus radiations from Nd:YAG lasers or other IR lasers, generally employed to generate ion acceleration from TNSA plasmas, can release high energy in such thin targets placed in vacuum. The thin foils give rise to forward plasma formation and high energy ion acceleration using intensities exceeding $10^{15}$ W/cm$^2$ and sub nanosecond laser pulse duration. The effect may be more relevant if the target surface is treated to reduce the reflectivity, modifying its roughness and morphology, and if the inner target contains special absorbent species, such as micro and nanostructures absorbent the high laser light.

In order to accelerate high energy protons, very hydrogenated targets, such as polymer based foils, can be irradiated. However, in order to obtain high plasma temperature and high ion energy the thin target must contain high electron density and must have high absorption coefficient. Such requisites can be found with metallic nanostructures embedded in the thin polymeric target. The use of polymeric structures containing CNT, with concentrations above 0.1 %, are very interesting for their capability to enhance the plasma hydrogen concentration due the CNT ability to absorb high hydrogen content [9].

![Figure 4. Absorption vs. wavelength for polyethylene pure and containing different nanostructures.](image)

Due to the high cost of CNT multiwall nanostructures, experimental investigations have demonstrated that also the use of amorphous carbon, as nanoparticles, may induce high IR absorption if embedded in polyethylene, with the advantage of the low cost of these targets. The targets prepared as discussed previously, offer a lot of applications to be employed at medium and high laser intensities in order to obtain high hydrogenated plasmas in high vacuum and high ion acceleration [10]. These “advanced targets” can be employed to produce protons at high energy and high yield for accelerator ion sources, for chemical modifications of polymeric surfaces, for hadron-therapy accelerating protons at high energy and for nuclear physics and astrophysics, permitting to produce many events of nuclear reactions. Measurements carried out during last run at PALS laboratory in Prague, irradiating by high intensity lasers ($10^{14-16}$ W/cm$^2$) thin mylar foils covered by thin metals, with respect to the uncovered film, have provided an significant enhancement of the plasma density, of above 40%. Plasma shows a significant enrichment in the proton content and an increase in the mean ion velocity for thin polymeric targets irradiated in TNSA approach containing gold nanoparticles, as many detectors connected in time-of-flight configuration have demonstrated [11]. Nanoparticles and nanostructures, in fact, show absorption bands in the visible and IR regions due to resonant plasmon absorption effects and to vibrational states of little atom clusters.
Thus, in conclusion, the enhancement of the absorption coefficients for polymers has been used to increase the plasma temperature ad density, the kinetic proton energy and the specific ion yield (protons, carbons,...) induced in the rear side of the TNSA target by sub-nanosecond pulses, as recently reported in our literature [12-13].

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