Fractal Carbon nanofoams by nanosecond and femtosecond pulsed-laser deposition

A. Pazzaglia*a, A. Maffini, D. Orecchia, M. Zavelani-Rossi, M. Passoni,

aEnergy Department, Politecnico di Milano, piazza Leonardo da Vinci 33, 20133 Milano, Italy

Abstract

We report on an investigation on the properties of ultra-low density, fractal, Carbon nanofoams fabricated with the nanosecond and femtosecond pulsed-laser deposition (PLD) techniques. We measure through innovative techniques the foam mean density and the properties of the fractal aggregates composing the film (i.e. nanoparticles diameter, fractal dimension, and gyration radius) as a function of several PLD process parameters, namely the background gas pressure and the laser pulse characteristics (energy, time duration, repetition rate). We discuss the experimental observation on the basis of the existing literature, and we propose an analytical equation, based on the fractal scaling law, to predict the foam density from the aggregates properties. Finally, we use analytical arguments to explain the observed trends in the nanofoam density with respect to the process parameters, useful to gain new insights on the nanofoam growth and to guide experimental work in fabricating ultra-low density films with precisely controlled properties.

Keywords: fractal, Carbon, nanofoam, pulsed-laser deposition, fs-PLD, ns-PLD

1. Introduction

Fractal nanofoams are peculiar low-density materials generated by the deposition onto a surface of fractal aggregates (FAs) composed by almost-spherical clusters, frequently named as nanoparticles (NPs). These films show interesting properties, such as ultra-low density, high surface area and fractal structure, which could be exploited for several applications, like supercapacitors [1], solar cells [2], super-amphiphobic coatings [3] and near-critical materials for laser-driven ion acceleration [4, 5] to name a few.

Even if fractal nanofoams can naturally occur, for example with impure Carbon composition during incomplete combustion processes as soot [6], only few techniques enable to fabricate them in a controlled environment. Pulsed-laser deposition (PLD) with nanoseconds duration pulses was successfully exploited to produce ultra-low density nanofoams with tunable composition (i.e. Carbon [7, 8], Tungsten oxide [9], Gold [10]). Since PLD is a very versatile technique with several deposition parameters and complex physical phenomena involved, it requires a thorough experimental and theoretical analysis for a controllable film production. PLD-produced Carbon nanofoam has been more deeply studied among all the possible compositions. It is featured by a high vacuum fraction, high specific surface area and unconventional magnetism [11].

In previous works, we have shown that the NPs composing the nanostructure are made by amorphous C, with a nearly pure sp2 network of topologically disordered graphitic domains [8]. The C foam density was measured with methods based on Energy Dispersive X-ray Spectroscopy (EDS) [12, 13], showing a steep dependence on the PLD gas pressure. In a recent investigation we proved that the material growth can be described by a ‘snowfall’ model [14]. In this framework, the laser ablates a Carbon target and the atomic species, expanding in a gas background, cool down and condensate in clusters with size of about tens of nm, called nanoparticles. The interaction with the background gas atmosphere also results in the sticking of these NPs into micrometric fractal aggregates through a process well

*Corresponding author. E-mail address: andrea.pazzaglia@polimi.it.
described by the cluster-cluster aggregation mechanism (CCA) [15]. Ultimately, FAs land onto a substrate and form a connected and open web to form a fractal film. Within this investigation, we also found that the aggregation time, which specify the dimension of the FAs and the foam properties, is roughly equal to the laser shot-to-shot time (inverse of the repetition rate), which is therefore another crucial deposition parameter.

Despite the number of works on this peculiar nanomaterial, a comprehensive study of all the deposition parameters and analytical arguments to provide a rationale to the foam density are still lacking. In particular, including other laser pulse characteristics, like the time duration (for example using femtosecond PLD, fs-PLD), could give access to novel control on the fabrication process.

Here we report an investigation on the production of fractal C nanofoams which fills the gap of the existing literature. In particular, we deposited Carbon nanostructures with different gas pressure, pulse fluence (near the ablation threshold), duration and peak power, using conventional PLD based on ns laser pulses and a more novel one based on fs pulses. We produced and characterized through innovative techniques either films (high deposition time) and separated FAs (low deposition time), and we explored their properties as a function of the above-mentioned parameters, demonstrating that the nanofoam density can be analytically determined from the properties of FAs. Finally, we discuss results from literature, and we propose an approximated analytical model that can accurately reproduce the experimental data and paves the way to further investigations and to a precise control of the deposited foams.

2. Methods

Carbon nanofoams reported in this article are produced with nanosecond and femtosecond pulsed-laser deposition (ns-PLD and fs-PLD respectively). The PLD technique employs a pulsed laser beam focused on a target, evaporating or otherwise removing target material at every pulse. The ablated species expand in a controlled background atmosphere, slowing down and forming the typical luminescent rounded shape region known as ablation plume. They continue to travel until they reach the substrate upon which the film is grown, located at a distance \( d_{ts} \) from the target. The main difference between the two techniques is due to the laser pulse duration and peak power: conventional ns-PLD exploits a laser pulse with temporal duration in the ns range to ablate a target, while the fs-PLD employs shorter sub-picosecond and higher peak power pulses. Moreover, the peculiarities of femtosecond laser technology have repercussions on the available range of the other deposition parameters: higher repetition rates can be achieved, but with lower pulse energy.

Our ns-PLD setup exploits the second harmonic (\( \lambda = 532 \text{ nm} \)) of a Q-switched Nd:YAG laser (pulse duration = 5 – 7 ns), with 10 Hz repetition rate and maximum pulse energy of 1 J. In the fs-PLD apparatus a commercial CPA Ti:Sapphire system (Coherent Astrella) delivers ultrafast pulses with temporal duration \( = 80 \text{ fs} \) and energy up to 5 mJ with 1 kHz repetition rate. In both setups the laser is focused on pyrolytic graphite targets with an incidence angle of 45°, and the film grows on single-crystal (100) Silicon wafer substrates. A circular on-axis target movimentation routine is employed, resulting in an annular ablation path.

In order to perform experiments with comparable deposition parameters for the two techniques, we set the fluence to three distinct values (180, 360, 540 mJ/cm²) for both ns- and fs-PLD; at the same time we kept fixed the mean power delivered by the laser source, given by the product of the pulse energy and the repetition rate (1.3, 2.6, 3.9 W respectively). Since there is a factor 100 between the repetition rate of the two laser systems, the same is true for the laser energies, and a factor of 10 is needed between the spot diameters to keep the fluence fixed. The pulse energy in the ns-PLD apparatus was thus set to \( E_p = 130, 260, 390 \text{ mJ} \), with a top-hat spot with a diameter of 8 mm, while in the fs-PLD one the energy was set to 1.3, 2.6, 3.9 mJ, with spot diameter (FWHM) equal to 0.8 mm. In both setups the background gas was Argon with pressure ranging between 25 and 250 Pa, and the target to substrate distance \( d_{ts} \) was fixed at 7 cm.

We performed two kind of depositions: first with long deposition time (10 min), which means many laser shots, to produce Carbon nanofoam films, and then with lower deposition time (30 s), few laser shots, in order to observe the single FAs composing the film. The first category of depositions was characterized in morphology by a Zeiss Supra 40 field emission scanning electron microscope (SEM, accelerating voltage 3 – 5kV). The electron microscope setup is also used to check deposit composition and density \( \rho_{\text{nf}} \), via a new method, called EDDIE, based on energy-dispersive x-ray spectroscopy (EDXS, accelerating voltage 3 – 5kV). It consists in a theoretical model, describing the
electron transport in the nanofoam/substrate system and subsequent characteristic x-ray emission, which enables to retrieve the film mass thickness from the measurement of the $K_{\alpha}$ peak intensity of Carbon (relative to the nanofoam) and Silicon (relative to the substrate) [13]. The average density of the nanofoam is then calculated as the ratio of the mass thickness and the average thickness, measured by SEM cross section images. The single aggregates (few laser shots) were deposited on transmission electron microscope (TEM) grids, and characterized by higher energy electrons (20 kV) on the same SEM setup, in order to increase the resolution with respect to the standard condition of Silicon substrate and lower accelerating voltage.

The few shot deposition samples have been used to measure the main fractal properties of the aggregates: the nanoparticles diameter $d_{np}$, the fractal dimension $D_f$ and the gyration radius $R_g$. The fractal dimension is a measure of the space-filling capacity of a pattern/system that tells how a fractal scales differently from the space it is embedded in [16]. The radius of gyration is another useful value for describing fractal patterns. It is defined as the radius at which a number of filled spaces equal to that of the entire pattern would have to be placed to have the same moment of inertia. These parameters are related to the total number of nanoparticles $N$ in the aggregate by the fractal scaling law [16]:

$$N = k \left( \frac{2R_g}{d_{np}} \right)^{D_f}, \quad (1)$$

where $k$ is a prefactor in the order of unity (Sorensen et al. found $k \approx 1.2$ via numerical and experimental arguments [17]). From the fractal scaling law (Eq. 1) also the FA density $\rho_a$ can be estimated with the following equation [18]:

$$\rho_a = \rho_{np} k \left( \frac{d_{np}}{2R_g} \right)^{3-D_f}, \quad (2)$$
where $\rho_{np}$ is the NP density.

The average nanoparticle diameter $d_{np}$ can be readily estimated from the aggregates 2D SEM images, employing the method developed by Dastanpour et al. [19]: it is based on the variation of the bidimensional pair correlation function at different distances from the aggregate main skeleton, applied to binarized images (we chose a threshold onto the correlation function equal to 0.8). Comparison with direct measurement of nanoparticle dimensions, directly from the raw SEM images, confirms the validity of the approach.

Since the fractal aggregates are inherently tridimensional in nature, the fractal dimension $D_f$ and the gyration radius $R_g$ can’t be obtained as easily from the 2D SEM images: the 2D projection transformation leads to a loss of information, especially for what concerns the aggregate geometrical properties [20]. In order to circumvent this issue we decided to simulate images of the FAs with an algorithm that enables to determine a-priori the aggregate characteristics (called ‘real’ $D_f$ and $R_g$). The 2D images are then processed to extract a measure of $D_f$ and $R_g$ to be compared with the exact (real) values.

Starting from the knowledge of the aggregate formation process (namely the snowfall-like aggregation model [14]) we developed an algorithm based on the cluster-cluster aggregation model (CCA), able to simulate the aggregate fractal structure [21]. A random number of spherical particles (up to 60 000) are placed in a box and can travel in any random direction (off-lattice) in a Brownian-like motion. When they come into contact with each other they have a certain probability of irreversibly stick together, forming a bigger aggregate, which is subject to the same random

![Figure 2: a) and b) show the calibration curve for the fractal dimension $D_f$ and the gyration radius $R_g$ respectively. The blue points coordinates are given by analytical calculation of the variable on the ordinata (real $D_f$ and $R_g$) and the measured one of the abscissa (with the box counting method for $D_f$ and the equivalent radius for $R_g$).](image-url)
motion itself. The process continues until a fractal aggregate containing all the primary particles is created. In order to better replicate the range of fractal dimension and gyration radius observed in actual experimental conditions, the number of primary particles was randomly sampled, and the sticking probability was randomly chosen each time (either 0.05 or 1). This last parameter is closely related to the aggregate fractal dimension: a higher sticking probability, close to one, leads to a more open structure, with lower fractal dimension (typical of diffusion-limited cluster-cluster aggregation, DLCA); on the other hand, a near zero sticking probability gives rise to a more compact structure, with higher fractal dimension, akin to reaction-limited aggregates (RLCA) [22]. The simulated images show a remarkable visual similarity with the real SEM images, as seen in Fig. 1 (SEM image) and b (simulation).

150 different aggregates were simulated with this procedure, and the resulting distributions of the real \( R_g \) and \( D_f \) are reported in Fig. 1 bottom panels (c and d).

This allowed us to construct linear calibration curves for the two quantities (Fig. 2), which can then be exploited to translate the measured 2D properties (obtained from the analysis of the aggregate SEM images) to their actual 3D value. We found a 15% error in the gyration radius determination, while a 5% error in the fractal dimension, which is around 0.1 in absolute if \( D_f \approx 2 \): this is enough to distinguish among DLCA processes \( (D_f \approx 1.8) \) and RLCA ones \( (D_f \approx 2.1) \) [23].

The measurement of the fractal dimension from the 2D images was carried out employing a box counting method, after image binarization. It is based on the self-similarity of fractal structures at different spatial scales: the image is subdivided in cells of a certain size, and the number of cells containing a nanoparticle against the size of the cell gives an estimate of the fractal dimension [24]. Other common methods for fractal dimension determination were tested, as power spectrum analysis and differential box counting, but the obtained relative errors were higher in comparison.

The gyration radius \( R_g \) is calculated as the radius of the circle with area equal to the aggregate effective area, which is obtained from the binarized aggregate image.

The determination of the aggregate fractal properties (i.e. \( d_{agp} \), \( D_f \) and \( R_g \)) was repeated on more than 10 different SEM images for each sample, each containing several NPs/FAs, in order to provide statistically significant results with their relative uncertainty.

3. Results

As mentioned in the introduction, we deposit and characterize several Carbon nanofoam films with different parameters of the PLD technique, namely the laser source (ns-PLD/fs-PLD), the pulse fluence, and the Argon pressure. We use a laser fluence near the ablation threshold, because it is a region where a higher NPs production and hence a better FA formation is expected [23], and a pressure in the range of tens to hundreds of \( Pa \), an appropriate region to produce to nanofoams, as indicated in previous works.

We measure for each film the mean density with the EDDIE method and we observe qualitatively the film morphology. Fig. 3 reports the results of the density characterization as a function of the Argon pressure and for different fluence and laser source (ns-PLD/fs-PLD). We also show in Fig. 4 some of the produced films top/side SEM images (for the ones with circled density values). By tuning the different PLD parameters, Carbon films with fractal features can be produced in a wide range of morphologies and density, ranging from near-bulk to ultra-low values (down to 5 \( mg/cm^3 \)). In particular, it should be noticed that, for both ns-PLD (Fig. 4a-c) and fs-PLD (Fig. 4d-f), for increasing pressure the film appears more and more open and with a higher inhomogeneity scale (notice the scale bars which widen for the bottom images).

| Pressure [Pa] | Fluence [mJ/cm²] |
|--------------|-----------------|
| ns-PLD       | < 125 (at 360 mJ/cm²) > 360 (at 100 Pa) |
| fs-PLD       | < 250 (at 360 mJ/cm²) > 180 (at 100 Pa) |

Table 1: Limits of the deposition parameters (on the Argon pressure and laser fluence) for the film growth within 20 minutes.

In addition, we observe that changing the laser source (ns-PLD/fs-PLD) different density trends are obtained with respect to the gas pressure and pulse fluence. Firstly, at 360 mJ/cm², where the majority of the data points are reported, the fs-PLD technique enables to produce Carbon films with a density trend very well described by a power law (with exponent equal to 2.2), while the nanofoams produced by ns-PLD have a density trend which drops rapidly with the
Figure 3: Mean density of Carbon films deposited with ns/fs-PLD and with variable Argon pressure and laser fluence. The scanning electron images of the circled data are shown in Fig. 4.

Figure 4: Scanning electron microscope images (top on the left and side on the right) obtained with deposition conditions reported in Fig. 3. The left panel (a-c) refers to ns-PLD films with pressure equal to 25, 50, 125 Pa respectively. The right panel (d-f) refers to fs-PLD films with pressure equal to 25, 100, 250 Pa respectively.

Argon pressure to a plateau, above 75 Pa, with constant density around 6 mg/cm$^3$. Another difference is found for the pressure deposition boundaries. Indeed no enough material is deposited on the substrate to form a continuous film, even at higher deposition time (20 min), at pressure higher than 125 Pa and 250 Pa for ns-PLD and fs-PLD respectively (see Table 1).
Secondly, we obtain a different behaviour of the film density at 100 Pa and variable laser fluence, with respect to the pulse duration. With the fs-PLD the nanostructure is more open at higher fluences, while for ns-PLD the density appears less dependent on this laser parameter. In addition, making reference to Table 1, the deposition rate is negligible for fluences lower than 360 mJ/cm² (for ns-PLD), and 180 mJ/cm² (for fs-PLD), suggesting that these values are near the ablation threshold. The lower ablation threshold in the fs-regime is consistent with literature works, as Ref. [25].

Due to all these observation, we can state that NPs-composed fractal films can be produced with controllable density by pulsed-laser ablation, through the tuning of several experimental parameters.

Since the Carbon nanofoams, as yet introduced, are formed by the landing on the substrate of FAs like in a snowfall, we expect that the Carbon nanofoam properties, like the mean density, are determined by the ones of their building blocks. Because, the FA density \( \rho_a \) depends on the NPs diameter \( d_{np} \), the gyration radius \( R_g \) and the fractal dimension \( D_f \) (Eq. 2), we analyse these quantities with proper samples deposition (with few shots) and through techniques illustrated in the Methods.

The result of the analyses are shown in Fig. 5. In detail, Fig. 5a-c reports the retrieved values of \( d_{np} \), \( D_f \) and \( R_g \) respectively, for ns-PLD and fs-PLD, for variable fluence, and Argon pressure fixed to 100 Pa. While Fig. 5d-f shows \( d_{np} \), \( D_f \) and \( R_g \) respectively, for variable Argon pressure, and fluence fixed to 360 mJ/cm².

It should be noticed that the two systems allow producing FAs with tunable properties. In particular both ns-PLD and fs-PLD generate NPs with a diameter between 12 and 5 nm, with a slight decreasing trend with respect to the fluence. Nevertheless, it is quite evident that the conventional ns technique produces nanoparticles with larger dimension, which also increases with the background pressure, as opposite to fs-PLD which shows an almost constant diameter with respect this parameter.

In addition, we observe, within the errors of the proposed method, that the fractal dimension is not influenced by the choice of the technique and the deposition parameters. Within the explored range of pressure and fluence, \( D_f \) assume a value of about 2 ± 0.1, which is consistent with several cluster-cluster aggregation mechanisms.

For what regards the gyration radius, we obtain in all the cases power-like distribution with a cut-off (see Fig. 6), as expected for cluster-cluster aggregation mechanisms [27]. In Fig. 5c,f we report the corrected mean equivalent diameter \( R_g \) and \( R_f \) respectively, for variable Argon pressure, and fluence fixed to 360 mJ/cm².

Since the properties of the grown film depend on the aggregate ones, we propose and extension of Eq. 2 to predict the Carbon nanofoam mean density \( \rho_{nf} \):

\[
\rho_{nf} = f_p \rho_a = f_p \rho_{np} k \left( \frac{d_{np}}{2R_g} \right)^{3-D_f},
\]

where \( f_p \) is the packing factor [28], which is a proportionality constant representing the fraction of the nanofoam volume occupied by the aggregates. As mentioned in the introduction, the NPs are composed by graphitic-like amorphous Carbon, thus \( \rho_{np} \) can be approximated by a near-bulk value, about 2 g/cm³ [29].

Combining Eq. 3 with the experimental data of \( R_g \), \( D_f \) and \( d_{np} \), we obtain foam density values represented in Fig. 7 where they are compared to the experimental values of the Carbon film densities. Here we fixed \( f_p = 0.15 \) by fitting the data with a root mean square error minimization. The obtained packing factor is lower than the one expected for solid spheres (0.51 – 0.64) [28], which is a reasonable result, since the FA branches generally extend well above the gyration radius, forming more open structures.

We emphasize that a remarkable agreement is found for all the points except the one at 25 Pa for ns-PLD, which is featured by NPs-assembled more compact film, without any trace of fractality (see Fig. 6). This confirms that Eq. 3 is able to accurately determine the nanofoam density, in a validity range given by the condition that a fractal structure is observed, therefore excluding the more compact film deposited at 25 Pa.

4. Discussion

In the Results we have confirmed that the Carbon nanofoam structure, produced by pulsed-laser ablation, is strongly dependent on the FAs properties. In particular, we have observed that, tuning the nanoparticles diameter,
Figure 5: Analysis on the single fractal aggregates (FAs). a-c report the nanoparticles diameter, the fractal dimension and the mean gyration radius of FAs with respect to the pulse fluence, for ns-PLD (blue) and fs-PLD (red). The ns-PLD points for 180 mJ/cm² fluence are not present because they lie under the ablation threshold. d-f report the same quantities with respect to the Argon pressure, for ns-PLD (blue) and fs-PLD (red). The fractal dimension (e) for the ns-PLD, 25 Pa point is not present since only single nanoparticles are deposited. Notice that the gyration radius for this condition (f) is equal to the nanoparticle radius for the same reason.

gyration radius and fractal dimension, we are able to control the meso-scale properties of the film, like the density.

The aggregate properties control can be operated by changing the Argon pressure, the laser fluence or by exploiting ns-/fs-PLD. The NPs diameter reaches the lowest value with the fs-PLD and it appears that this value is quite independent with respect to the gas pressure, as opposite to the ns-PLD where \( d_{np} \) increases with the pressure, as yet reported in the literature [30]. This difference arises due to the different NPs formation mechanisms. In the ns-PLD regime, the clusters form because the atomic species super-saturate the gas and condensate [31], while in the fs-regime they are directly ejected from the target through spinodal decomposition [32, 33]. We also obtained for both the techniques a decreasing trend of \( d_{np} \) as a function of the fluence, which is in agreement with literature theoretical and experimental arguments ([25]).

We have also found that the aggregates fractal dimension is constant (about 2 ± 0.1) within our error bars. This value is consistent with different aggregation mechanism, as RLCA, BCA, and even an hybrid DLCA-RLCA, where the sticking probability is intermediate between 0 and 1. More accurate measurements, which are beyond the scope of this work, should be performed to discriminate between those mechanism. 2 ± 0.1 is comparable, albeit being slightly higher, with 1.8 found with ns-PLD deposition at very high fluence (1600 mJ/cm²) [14]. This difference might be due
Figure 6: Gyration radius $R_g$ distribution, obtained with $100\, \text{Pa}$, $360\, \text{mJ/cm}^2$ and ns-PLD (a) and fs-PLD (b). Notice that the shape can be interpreted both as an exponential or a power law with cut-off.

Figure 7: Comparison between the foam density obtained experimentally from Carbon films and the one calculated by Eq. 3, exploiting the fractal aggregates properties reported in Fig. 5 (the error bars are calculated by propagating the uncertainty). a) shows this comparison as a function of the pulse fluence, while b) as a function of Argon pressure.
to a higher sticking coefficient at the higher plume temperatures, obtained at higher fluence.

For what regards the gyration radius, we obtained that ns-PLD is capable of producing higher values at equal deposition condition, which means that a higher number of nanoparticles can stick together in the vacuum chamber before the aggregate lands on the substrate.

Within the cluster-cluster aggregation models, this behaviour is justified by an aggregation with longer time or higher sticking rate. Indeed the gyration radius scales with the mean number of NPs per aggregate \( S \), also called size, \( (R_g \propto S^{1/D_f}) \), and the size increase with time with the following power law [34, 35].

\[
S(t_{agg}) \propto (t_{agg}/t_0)^z, \tag{4}
\]

where \( t_{agg} \) is the aggregation time, \( z \) an exponent which varies greatly as a function of the FAs diffusivity, the NPs sticking probability and the specific aggregation mechanism [16, 23], and \( t_0 = 3\eta/8k_BT_c \) the characteristic time, which indicates the rate of single clusters collision (with \( \eta \) the gas viscosity, \( k_b \) the Boltzmann constant, \( T \) the gas temperature and \( c_0 \) the initial number concentration of particles, defined as the ratio of the total number of clusters and the volume of aggregation).

The mean aggregate size \( S \) is particularly important in the determination of the nanofoam structure. Indeed \( \rho_{nf} \) explicitly depends on \( S \), through Eq. [3], which can be approximated exploiting the fractal scaling law \( (S = k(2R_g/d_{nf})^D) \) and assuming \( D_f = 2 \) as follows:

\[
\rho_{nf} \approx f_p \rho_{np} k \frac{d_{nf}}{2R_g} \approx f_p k^{3/2} \rho_{np} \frac{1}{\sqrt{S}} \tag{5}
\]

As a consequence, the different nanofoam properties are simply related to the mean FAs size. As mentioned above, \( S \) depends on the specific aggregation mechanism, through the exponent \( z \), the characteristic time \( t_0 \) and the aggregation time \( t_{agg} \), which, ultimately, are controllable by the PLD deposition parameters.

In particular, we can make some estimations to directly relate the aggregate size to the laser fluence and pressure. First, the NPs concentration \( c_0 \) can be written as \( M_{np}^{tot}/m_{np}V_{agg} \propto M_{np}^{tot}/\rho_{np}d_{np}^3V_{agg} \), where \( m_{np} \) is the nanoparticles mass, while \( M_{np}^{tot} \) is the total mass ablated by one laser pulse and which condensate into NPs, and \( V_{agg} \) is the volume where the nanoparticles aggregate. This volume should be roughly proportional to the plume volume \( V_p \), that can be approximated by the one derived with the blast wave model \( V_{agg} \propto V_p \propto E/p \) [36, 37], with the \( E \) the pulse energy absorbed by the target and \( p \) the background gas pressure. By combining these calculation, we can estimate the characteristic time with:

\[
t_0 = k' \frac{\eta \frac{E}{p} \rho_{np}d_{np}^3}{k_B T p} M_{np}^{tot}, \tag{6}
\]

with \( k' \) a numeric constant. Plugging Eq. [3] into Eq. [5] and using the characteristic time (Eq. [6]), we finally retrieve:

\[
\rho_{nf} \propto \rho_{np} \left[ \frac{\eta \frac{E}{p} \rho_{np}d_{np}(E/p)^{3/2}}{k_BT p M_{np}^{tot}(E/p) \frac{1}{\tau_{agg}(RR)}} \right]^{2/3} \tag{7}
\]

where we explicitly taken into account the possible dependencies of \( d_{np} \) and \( M_{np}^{tot} \) onto the laser energy and the gas pressure, and we hypothesized that the aggregation time depends only on the laser repetition rate \( RR \), as stated in Ref. [14].

Eq. [7] is obtained under several approximations and it is not meant to be predictive, yet it enables to justify some of the experimental observations here reported.

Firstly, we have seen from Fig. [5] that the NPs size produced by fs-PLD is quite independent on the pressure since their formation mechanism takes place only in the target, and therefore we can consider that also the total cluster mass depends only on the pulse energy. Thus, keeping the pulse energy constant and variable gas pressure, we obtain from Eq. [7] that \( \rho_{nf} \propto (1/p)^{3/2} \) which predicts a power law, experimentally observed in Fig. [7]. On the other hand, the cluster formation in ns-PLD is highly influenced by the gas conditions, since they are formed by condensation into the atmosphere, and the general dependence reads as \( \rho_{nf} \propto \left[ d_{np}(p)^{3/2}/p M_{np}^{tot}(p) \right]^{2/3} \). This justifies the peculiar trend of the ns-PLD-produced Carbon nanofoam density with the pressure. Indeed, with the conventional ns technique, \( \rho_{nf} \) rapidly drops to low values for increasing pressure, due to the more efficient cluster formation (at low pressure the gas
temperature is hotter, eventually inhibiting NP formation \([25]\)) and then the slope reduces due to the increase of the NPs size, which arises raised at the third power.

Secondly, if we focus our attention on the dependence of Eq. \(7\) on the laser fluence (with constant pressure), we notice that \(\rho_{nf} \propto \left[\frac{E_{d}}{M_{nf}^{nf}}(E)\right]^{\frac{1}{2}}\). We observe from Fig. \(5\) that the NPs size has a slight dependence on the fluence, for both fs-PLD and ns-PLD. \(M_{nf}^{nf}(E)\) is more difficult to model, but we can approximate it as proportional to the ablation rate, which instead is frequently reported in the literature.

Indeed, the ablation rate from ns-duration pulses follows a linear relation with fluence \([38]\), which therefore elides with the numerator and justifies the slight dependence of \(\rho_{nf}\) on \(F\) for ns-PLD (see Fig. \(7\)). Conversely, it was observed that, for fs-duration pulses, the ablation rate grows with a power law (with exponent higher than 1) in the range \(70 \sim 300 \text{mj}/\text{cm}^2\) \([39]\). This is in agreement with the pronounced decrease in the Carbon nanofoam density with the fluence of Fig. \(7\).

Moreover, we point out from Eq. \(7\) that also \(\tau_{agg}\) plays an important role in determining the nanofoam structure. This time should be roughly equal to the shot-to-shot time (inverse of the laser repetition rate) \([14]\), suggesting that lower laser repetition rates should result into lower density films at equal conditions. Our ns-PLD operates at 10 Hz repetition rate (100 \(\text{ms}\) shot-to-shot time), while our fs-PLD at 1 \(kHz\) (1 \(\text{ms}\) shot-to-shot time), which are typical values for commercial systems. We confirm through our experimental observations that lower density values are obtained for higher shot-to-shot times (ns-PLD) with respect to lower ones (fs-PLD), when the Argon pressure and fluence is fixed. The difference in \(\tau_{agg}\) for 10 Hz and 1 \(kHz\) PLD also reflects on the FAs mean gyration radius, because \(R_{g} \propto S^{1/D_f} \propto \tau_{agg}^{1/D_f}\), predicting a factor of about 10 between the radius of ns-PLD and fs-PLD. This argument gives an explanation why, for equal deposition parameters, Fig. \(5\) (ns-PLD) shows a distribution which extends to values of about 10 times the ones of Fig. \(6\) (fs-PLD).

Finally, Eq. \(7\) should be applicable in principle to different composition nanofoams, even if further investigation should be carried out. Under this hypothesis, the NP density plays a crucial role since \(\rho_{nf} \propto \rho_{np}^{2+1}\), and materials with higher bulk density should produce, at equal parameters, higher density films.

5. Conclusion

In conclusion, we have presented a comprehensive investigation on the production and analysis of Carbon nanofoams by pulsed-laser deposition technique as a function of several parameters, namely the gas pressure and the laser pulse characteristics (i.e. the pulse fluence, time duration and repetition rate).

We showed that films in a wide range of density, from \(\approx 1200 \text{mg/cm}^3\) to \(\approx 5 \text{mg/cm}^3\), and with a great variety of morphology can be fabricated by using different deposition conditions. Moreover, we compared the foams produced by a conventional PLD with ns duration pulses and by a more novel one with fs duration. We obtained that the film density produced through ns-PLD has a steep trend with a plateau as a function of the gas pressure, while the fs-PLD one is featured by a power law trend, which makes this technique more appropriate for a finer control of the film density.

By a thorough characterization with innovative procedures of the single aggregates composing the nanofoam, we demonstrated that the mean density depends on FA properties, namely the gyration radius, fractal dimension and nanoparticles size (Eq. \(3\)). Also in this case we compared the results obtained with the ns-PLD and the fs-PLD. The first enables to fabricate bigger aggregates, while the second is able to produce smaller NPs, with no appreciable dependence on the gas pressure.

Finally, we proposed an approximated scaling law based on analytical arguments (Eq. \(7\)) that can explain and reproduce all the observed trends in the nanofoam density with respect to the deposition parameters.

Overall our study indicates that a precise control on carbon nanofoams characteristics can be obtained, through a correct choice of the PLD deposition parameters, mainly the gas pressure and the pulse fluence. Moreover, our investigation highlights the differences between the two typical PLD systems, namely ns- and fs-PLDs. Altogether, this paves the way for a reliable production, even of nanofoam composition other than Carbon, which will beneficial in a wide range of applications/fields.

References

[1] B. Zhang, D. Wang, B. Yu, F. Zhou, W. Liu, Candle soot as a supercapacitor electrode material, RSC Advances 4 (6) (2014) 2586–2589.
[39] M. Lenner, A. Kaplan, C. Huchon, R. E. Palmer, Ultrafast laser ablation of graphite, Physical Review B 79 (18) (2009) 184105.