Evidence of diffusive fractal aggregation of TiO$_2$ nanoparticles by femtosecond laser ablation at ambient conditions

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Keywords: fractal nanostructure, diffusion limited cluster aggregation, laser ablation

Supplementary material for this article is available online

Abstract

The specific mechanisms which lead to the formation of fractal nanostructures by pulsed laser deposition remain elusive despite intense research efforts, motivated mainly by the technological interest in obtaining tailored nanostructures with simple and scalable production methods. Here we focus on fractal nanostructures of titanium dioxide, TiO$_2$, a strategic material for many applications, obtained by femtosecond laser ablation at ambient conditions. We compare a theoretical model of fractal formation with experimental data. The comparison of theory and experiment confirms that fractal aggregates are formed after landing of the ablated material on the substrate surface by a simple diffusive mechanism. We model the fractal formation through extensive Monte Carlo simulations based on a set of minimal assumptions: TiO$_2$ nanoparticles arrive already formed on the substrate, then they diffuse in a size/mass independent way and stick irreversibly upon touching, thus forming fractal clusters. Despite its simplicity, our model explains the main features of the fractal structures arising from the complex interaction of large TiO$_2$ nanoparticles with different substrates. Indeed our model is able to reproduce both the fractal dimensions and the area distributions of the nanostructures for different densities of the ablated material. Finally we discuss the role of the thermal conductivity of the substrate and the laser fluence on the properties of the fractal nanostructures. Our results represent an advancement towards controlling the production of fractal nanostructures by pulsed laser deposition.

Introduction

Fractal structures are commonly found in different natural processes [1]. While their geometrical features are quite universal, the mechanisms of their formation can be very different. In view of the technological applications, fractal nanostructures at the nanoscale have been widely investigated in surface science. They are at the base of recent proposals for sensing devices [2] and optical devices [3]. The realization of fractal nanostructures would also allow enhancing the selectivity behavior of catalyst material with high porosity [4] or to increase the performances of super-capacitors [5]. Understanding the mechanism of fractal nanostructures formation with the aid of theoretical models is an essential step towards building engineered microdevices with tailored properties.

Fractal nanostructures have been obtained on various substrates, by deposition of the target material ejected as a plume due to the laser ablation process [6, 7]. This technique, known as pulsed laser deposition (PLD), has been used in various environments (liquids, high gas pressures) and with different laser pulses characteristics (pulse length, wavelength, fluence, polarization). Fractal aggregates obtained from thousands of nanosecond
pulses have been demonstrated in water [8] and at high argon pressure [9, 10]. When the laser pulse duration is
reduced to less than a picosecond, PLD enters in the femtosecond regime (fs-PLD), and a different physical
mechanism for ablation sets in [11]. In this case, since the pulse duration is shorter than the electron–phonon
relaxation time, which is of the order of few picoseconds, the ablation mechanism is not due to thermal melting
as in the nanosecond case. Fractal nanostructures in the fs-PLD regime have been reported in different
conditions [6, 7, 11–15].

Various formation mechanisms have been conjectured for fractal nanostructures in PLD experiments: they
could form in flight during the plume expansion [16] or by nanoparticle diffusion and aggregation on the surface
[7] or in both ways. In the literature it was suggested that diffusion of the ablated material after landing should
play an important role in the fractal formation. Such conclusion were based on the fact that the fractal dimension
of the aggregates [7] found in PLD experiments is compatible with the fractal dimensions obtained in numerical
experiments with diffusion models of nanoparticle aggregation. On the other side fractal dimension is not a very
sensitive quantity: fractals obtained by very different mechanisms can have the same fractal dimension. For these
reasons different indicators to sort out fractal dynamics are needed, such as the area distribution of fractal
nanostructures, which, together with the fractal dimension, can help to discriminate between different
formation mechanisms.

Here we analyze experimental data of titanium dioxide (TiO$_2$) nanostructures obtained by fs-PLD in air at
ambient conditions on different substrates. TiO$_2$ is a strategic material in many technologically important areas,
such as heterogeneous catalysis [8, 17, 18], photo-assisted oxidation [19], optical [20] and photovoltaic [21]
devices. In [12], fractal structures formed by spherical TiO$_2$ nanoparticles on silicon substrate, with an average
diameter below 20 nm have been synthesized. These nanoparticle have ordered edges forming polygons,
suggesting that they are crystalline. We analyze the structures found on different substrate and we present
further data on the silicon substrate. Here we show that, under the same experimental conditions (laser fluence,
pulse duration, polarization, distance of the target from the substrate, see methods), different nanostructures are
formed on different substrates, ranging from single nanoparticles on graphite, ramified fractuals on silicon and
long fractal chains on quartz. This confirms that processes occurring on the substrate, after landing of the
ablated material, are essential to explain the nanostructures formation. We propose a mechanism for fractal
formation in which single nanoparticles, formed during the ablation process or during the plume expansion,
land on the substrate and then diffuse and aggregate to form larger nanostructures of fractal dimension. We
simulate nanoparticle diffusion and aggregation using a diffusion limited cluster aggregation (DLCA) model
[22, 23]. DLCA models have been extensively used in literature and they can vary in many specific features, such
as dependence of diffusion on the nanoparticle size, degree of reversible aggregation, etc. In our simulations,
instead of three-dimensional nanoparticles, we consider two-dimensional nanoparticles of circular shape which
are able to diffuse on a two-dimensional surface. Our diffusion model is based on a set of minimal assumptions:
irreversible sticking and size/mass independent diffusion probability of the nanoparticles, see figure 1.

The initial nanoparticle area distribution, from which substrate diffusion calculation starts, is retrieved from
the experimental data. To this end we extract the diameter of the nanoparticles from the HOPG substrate where
nanoparticle aggregation is negligible and the initial distribution is composed mainly of single nanoparticles
figure 2(a). From this initial nanoparticle area distribution, the DLCA algorithm is able to reproduce the main
qualitative and quantitative experimental features for other substrates (silicon, quartz, figures 2(b), (c)), where
nanoparticle aggregation is essential to explain the observed experimental distribution, by changing only the
simulation time.

The fractal structures obtained numerically look very similar to the experimental ones. Moreover our model
reproduces not only the fractal dimensions of the nanostructures, but also their area distribution for different
densities of the ablated material on the silicon substrate, where most of our experimental data are collected.

Fractal formation has been widely analyzed in the context of vapor phase epitaxy [24, 25]. In this case, fractal
structures are composed of single atoms which are adsorbed on the surface from the gas phase, in vacuum and at
very low temperature. After the deposition, fractal aggregates are obtained by thermal diffusion of single atoms,
which move in a random walk until they stick irreversibly to another growing aggregate. In this context also the
mechanism of diffusion of large two-dimensional islands of adsorbed atoms or vacancies have been analyzed
[26]. The situation is different and more complicated in the case of PLD at ambient conditions where hot three-
dimensional nanoparticles with a crystalline structure, containing several thousands atoms [12] land on a room
temperature (RT) substrate. We find to be striking that our simple diffusion model is able to adequately describe
fractal structures obtained in PLD experiment. In particular the effectiveness of a size-independent diffusion
mechanism is particularly intriguing, see discussion section for more details.
Figure 1. Main three steps of the Monte Carlo Method implemented to reproduce fractal structures found experimentally. (i) Instead of the spherical three-dimensional nanoparticles found in the experiment we consider two-dimensional circular nanoparticles which are extracted from the experimental area distribution. Panel (a) shows the histogram of the initial probability density distribution \( P(A) \) of \( 5 \times 10^4 \) single TiO\(_2\) nanoparticles areas \( A \) extracted from experimental data obtained on HOPG substrate, see figure 2(a). The histogram is normalized so that \( \int_0^\infty P(A) \, dA = 1 \). The fitting formula (blue curve) is given in equation (1) and normalized as the histogram. (ii) Circular nanoparticles of different sizes, extracted from the probability distribution \( P(A) \), are randomly distributed on a two-dimensional surface and let diffuse isotropically in the four main directions, see panel (b). (iii) When touching nanoparticles aggregate irreversibly. The cluster thus formed can also diffuse with a size independent probability and aggregate irreversibly when touching, see panel (c). The process is halted when the same number of clusters per unit area of the experimental images is reached. For more details see text.

Figure 2. SEM images (5.6 × 5.6 \( \mu\)m\(^2\)) of TiO\(_2\) deposited on HOPG (a), silicon (c) and quartz (e) by fs-PLD, are compared with results of numerical simulations. In panels (b), (d) and (f) we show the Monte carlo simulations obtained with the diffusive model at the same coverage. The numerical simulations shown have been made on a grid of 800 × 800 pixels and at different coverages, corresponding to the experimental images. Transparency were used in the simulated images to make them more similar to the experimental one.
Table 1. Fractal dimension $D_f$ of numerical simulations are compared with experimental ones. For the HOPG, there are no fractals, so that $D_f = 1$ both for the experimental and the numerical case. For the case of TiO$_2$ on quartz the $D_f$ has been computed for the fractal structures along the defect only.

| Substrate/coverage | Experimental fractal dimension | Numerical fractal dimension |
|--------------------|-------------------------------|----------------------------|
| TiO$_2$ on Silicon 10% coverage figures 2(c), (d) | 1.42 | 1.36 |
| TiO$_2$ on Silicon 20% coverage figures 3(b), (c) | 1.44 | 1.45 |
| TiO$_2$ on graphite 6% coverage figures 2(a), (b) | 1 | 1 |
| TiO$_2$ on quartz 5% coverage figures 2(e), (f) | 1.23 | 1.32 |

Results and discussion

In figures 2(a), (c), (e), experimental images of TiO$_2$ nanostructures obtained by fs-PLD on different substrates are shown. The deposition of TiO$_2$ by fs-PLD under the same experimental conditions, results in very different nanostructures depending on the substrate types, indicating that the substrate is playing a main role in determining the aggregation behavior. The fractal dimension $D_f$ of the nanostructures was computed using the counting box method described in methods. Results are reported in table 1.

On HOPG (figure 2(a)), we observe no fractal nanostructures, apart from very small aggregates of few nanoparticles. The distribution on HOPG is composed mainly of single nanoparticles with diameters ranging from 6 to 7 nm up to more than 100 nm, see histogram plotted in figure 1(a). On silicon (native silicon oxide, figure 2(c)), we observe fractal aggregates randomly ramified, composed of nanoparticle with a similar range of diameters. On quartz we observe an unexpected behavior: structures very similar to one-dimensional chains, composed of aggregated nanoparticle, figure 2(e), with a fractal dimension (see table 1). Such chains are extending up to almost a mm of length with a lateral dimension of few nm, with a length/width ratio up to five orders of magnitude, see online supplementary figure 6 in methods.

These data strongly suggest that nanostructures are not formed by aggregation of nanoparticle during the plume expansion from the target material to the substrate surface, but they are rather the result of an aggregation mechanism which occurs after landing of the ablated material on the substrate. This experimental evidence is the starting point for our model of the nanoparticle based structure formation. We assume that after ablation, nanoparticle of different diameters land on the substrate with a random spatial distribution. The initial distribution of nanoparticle diameters for all type of substrates has been obtained by fitting the experimental area distribution obtained from the HOPG samples, see figure 2(a), where surface aggregation is playing a negligible role. For the TiO$_2$ nanoparticle area distribution, shown in figure 1(a), we obtained the following fitting bi-exponential law:

$$P(A) = P_1 e^{-A/A_1} + P_2 e^{-A/A_2},$$

where $A$ is the nanoparticle area in nanometers squared and $P_1 = 5.58 \times 10^{-4}$ nm$^{-2}$, $P_2 = 5.58 \times 10^{-6}$ nm$^{-2}$, $A_1 = 1700$ nm$^2$, $A_2 = 9200$ nm$^2$.

After landing on the substrate surface, we further assume that nanoparticles can diffuse and aggregate to form clusters. We described such process with a diffusion and aggregation model, belonging to the class of DLCA models [22, 23], which we implemented using Monte-Carlo simulations. The algorithm we used is based on a set of minimal assumptions, see also figure 1, and it can be described as follows:

1. We simulate the impinging ablation plume on the substrate with circular two-dimensional nanoparticles with a random distribution. The nanoparticle diameter distribution is taken from experiment and it is given by the fitting formula equation (1). The nanoparticles low-diameter cut-off is set to 5 nm, that is the smallest diameter observed experimentally. Circular nanoparticles are characterized by a center and a radius. If the initial deposition yields two or more nanoparticles touching each other, they are counted as a larger cluster.
All the nanoparticles belonging to the same cluster will move altogether thereafter. Indeed a nanoparticle can never leave or move within the cluster it belongs to, so that clusters can only increase in size but not decrease. At first most clusters are formed by only one nanoparticle and the total number number of clusters is counted.

2. The clusters, which can be composed by one or more nanoparticles, can diffuse isotropically on the substrate surface. Diffusion is simulated by giving each cluster the possibility to move with a finite probability at each Monte Carlo step. Clusters cannot be deformed or rotated, but can only translate with equal probability in one of the four directions (up–down, left–right) on the surface. The probability to move in one direction is $p/4$, so that at every time step, each cluster has a probability $p$ to move and $1 - p$ not to move.

3. When two clusters touch, they stick together irreversibly, forming a new cluster. At the end of each Monte Carlo step the number of clusters is counted again. Clearly for very long times all the nanoparticles aggregate in a single large cluster.

4. We assume that each cluster diffuse with a size/mass independent probability. We checked also the effect of a size–dependent probability of moving, see discussion below.

5. In order to compare numerical simulations with experimental data, the simulations are halted when the same number of clusters per unit area present in the experimental images is reached. Note that this choice implies that the numerical results are independent of the precise value of $p$ used in the simulations.

Examples of the numerical results obtained with our model for diffusion and aggregation, are shown in figures 2(b), (d), (f) and can be compared with experimental SEM images shown in the upper panels of figure 2. The numerical results show a good qualitative resemblance to the experimental image.

When TiO$_2$ is deposited by fs-PLD on HOPG, the experimental data in figure 2(a) show that no aggregates are formed and the fractal dimension is $D_f = 1$. A random deposition of nanoparticles without diffusion, following the probability distribution expressed in equation 1, reproduces the experimental data, see figure 2(b).

On the other side, in order to reproduce the ramified fractal structures obtained on the silicon substrate, we used our model of diffusion and aggregation of nanoparticles. The numerical results are shown in figure 2(d) for the low coverage case (10%) and should be compared with the experimental image in figure 3(c). The fractal dimension is near the value found from the experimental distribution, see table 1. To reproduce the long fractal chains found on quartz substrate, see figure 2(e) and online supplementary figure 6, we modified our diffusive model further assuming that on the surface there is a defect represented by a line in a given direction. When a cluster reach such line, diffusion is halted for that cluster, which can however grow if smaller clusters reach it. The result of numerical simulations within this assumption is shown in figure 2(f). For this case we chose a line defect with the same direction of the fractal chain in the experimental image, see figure 2(e).

In order to highlight the effect of diffusion and to rule out the possibility that fractal structures could be formed by aggregation of nanoparticle upon randomly landing on the surface, without diffusion, we analyze in figure 3 the case of TiO$_2$ fs-PLD on silicon at high coverage (20%). The result of a numerical simulation where only random deposition of nanoparticles without diffusion and aggregation is shown in figure 3(a). The result is clearly different from the experimental data in figure 3(c), which instead well resembles our numerical results including diffusion in figure 3(b). This further confirms that the nanoparticle diffusion is essential to reproduce the experimental results.

We have also simulated the case of a single large cluster, see figure 4. By comparing the experimental image in figure 4(a) with numerical simulation in figure 4(b) one can note that the simulation is able to reproduce the aggregation pattern very well down to the smallest nanoparticle.

Note that the fractal dimensions of the simulated nanostructures are in good agreement with the fractal dimension of the experimental images, see table 1. As already stated in the Introduction, different mechanism of fractal formation can lead to structures with similar fractal dimension. Thus we consider the area distribution of the nanostructures as a further test for the theory. The experimental data on silicon are a good benchmark since a large statistics is available for the area of the nanostructures for different coverages. In figure 5, the area distributions obtained for two different coverages on silicon, are compared with the numerical results. The distribution obtained numerically (red circles) is in good agreement with the experimental distribution, showing the effectiveness of our model. For the 20% coverage case, shown in figure 5(b), the algorithm overestimates the probability for clusters with large area. This difference could be explained by the fact that experimentally 150 laser pulses have been used to obtain the sample, see methods. Each pulse is separated by 1 ms, a time probably sufficient for the nanoparticles to thermalize. In our simulations we neglected the effect of such multiple depositions, which can become relevant at higher coverages. Indeed for large coverage newly arriving
nanoparticles are more likely to land on pre-existing clusters, resulting in a smaller area of the final fractal structures.

In order to highlight the importance of the diffusive mechanism, we also reported in figure 5 the distribution of the nanostructures obtained just after the random deposition of nanoparticle on the surface, before diffusion (blue curve). The result clearly show that diffusion is essential to reproduce experimental data.

The assumption of a size independent diffusion might appear counterintuitive, since larger cluster are expected to diffuse less than smaller clusters. In order to check this assumption, we compared the experimental data with numerical results obtained using a size dependent diffusion probability. At variance with the size independent diffusion model, now nanoparticles and clusters of different sizes have different probability to move. We implemented a model in which smaller particles are more likely to move. Assuming that the mass of clusters is proportional to their area, we modified the probability to move \( p \) as \( p \propto \frac{A_0}{A} \), where \( A_0 \) is the area of the smallest nanoparticle and \( A \) is the area of the cluster we want to move. As in the previous cases, we halt the

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Figure 3. Numerical simulations are compared with experimental images of TiO\(_2\) deposited on silicon by fs laser ablation. Left panel: Monte Carlo simulation of the initial distribution of nanoparticles without diffusion with the same coverage of the experimental image shown in the right panel. Central panel: Monte Carlo simulation obtained with the diffusive model described in the text at the same coverage of the experimental image. Right panel: part of a SEM image of TiO\(_2\) clusters over a silicon surface with a resolution of 7 nm per pixel and a coverage of about 20%. The numerical simulations are implemented on a grid of 800 \( \times \) 800 pixels. Transparency were used in the simulated images to make them more similar to the experimental one.

Figure 4. (a) SEM image of TiO\(_2\) clusters on silicon surface with a resolution of 2 nm per pixel and about 20% coverage (b) simulation made on a grid of 768 \( \times \) 1024 pixels at 20% coverage. The fractal dimension of the experimental cluster \( D_e \approx 1.36 \) is very close to the fractal dimension of the cluster obtained with our numerical simulation, \( D_f \approx 1.4 \). Note that the nanoparticle observed experimentally are spherical (three-dimensional) and they present a faceted morphology, indicating a crystalline structure, while the simulated nanoparticle are circular (two-dimensional). Transparency were used in the simulated image to make it more similar to the experimental one.
simulation when the same number of clusters per unit area of the experimental images is reached. The fractal
dimension obtained with the size dependent model is in reasonable agreement both with the fractal dimension
obtained from experimental data and with the fractal dimension obtained with the size independent model: for
the case of 10% coverage we obtain $D_f = 1.37$, while for the case of 20% coverage, we obtained $D_f = 1.49$
(see table 1 for a comparison with experimental data and simulation with the size independent diffusion model).
This confirms that fractal dimension is not very sensitive to the specific mechanism of fractal formation. On the other
side, the area distribution obtained with the size dependent diffusion model (see figure 5), does not agree with
experimental data: the area distribution is more uniform with a lower number of smaller clusters and a larger
number of big clusters with respect to the experimental data. These features are common to any size dependent
diffusion mechanism. Indeed, they can be explained with the fact that large clusters have a small probability to
move so that growth occurs around many aggregation centers. This result shows that the assumption of the size
independent diffusion reproduces the experimental results in a better way.

Discussion

The data presented here give evidence that fractal nanostructures obtained on different substrates by fs-PLD of
TiO$_2$ in air and at RT are formed by diffusion of the deposited nanoparticle on the surface. To rationalize these
findings, we propose a possible substrate-dependent mechanism of diffusion.

In PLD fractal structures are formed by three-dimensional nanoparticles with different diameters
containing several thousand atoms [12]. The ablated material has a very high temperature when it arrives on the
substrate: the thermal energy is stored in each nanoparticle due to the mechanism of plume generation [27].
After deposition it is reasonable to assume that diffusion continues at a relevant rate until thermalization
between nanoparticle and substrate, which is at RT, occurs. Under the same experimental conditions (laser
fluence, distance of the substrate from the ablated target material, etc) the nanoparticle initial temperature will
be the same on the different substrates. Thus the properties of the fractal structures will be strongly influenced by
the time the nanoparticle need to thermalize with the substrate and consequently on its thermal conductivity.
We can expect a fast thermalization and small fractals for substrates with large thermal conductivity, while a slow
thermalization and the formation of large fractals for small thermal conductivity substrates. This scenario is
consistent with the experimental results shown here, see (figure 2) and in (supplementary figure 6). For HOPG,
which has a large in-plane thermal conductivity ($\sigma_{\text{HOPG}} = 1700 \text{ W (m K)}^{-1}$), the ablated nanoparticle do not
form any cluster. In the case of quartz, with thermal conductivity ($\sigma_{\text{SiO}} = 1.4 \text{ W (m K)}^{-1}$) three order of

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Figure 5. Comparison between the area distributions of fractals obtained in numerical simulations and the area distribution of fractals
found experimentally on silicon substrate for different coverages. (a) 10% coverage case: black histogram is the area distribution
extracted from 2245 clusters deposited on an overall area of 1081 µm$^2$ (seven single images with an area of 155 µm$^2$), while red circles
show the result of numerical simulations extracted from 1599 simulated clusters. (b) 20% coverage case: black histogram is the area
distribution extracted from 23869 clusters deposited on an overall area of 6030 µm$^2$ (19 single images with an area of 317 µm$^2$), red
histogram is extracted from 2998 simulated clusters. In both panels, as blue crosses the area distribution obtained with the size-
dependent diffusion mechanism is shown, see text for more details. As a blue dashed curve the distribution of the cluster area obtained
just after randomly depositing the nanoparticles on the surface and without diffusion is also shown.
magnitude lower than HOPG, we observe the formation of chains up to hundreds of μm long, see (figure 6) in supplementary material. For silicon, which has an intermediate thermal conductivity ($\kappa_s = 70$ W (m K)$^{-1}$), we have the formation of clusters with sizes in between the two preceding cases. The connection between the properties of fractal aggregates and the thermal conductivity of the substrate is very intriguing and further experimental data and theoretical work are needed to analyze the relevance of the substrate thermal conductivity. The above discussion also suggests that fractal aggregates size should depend on the laser fluence since this parameter will impact the initial temperature of the ablated nanoparticles at landing and might also impact their area distribution.

The interpretation of our results is based solely on the role of thermal conductivity. We have neglected the influence of the substrate roughness and substrate charging (except for the hypothesis on quartz), for the following reasons: (1) the substrate rms roughness is the lowest for HOPG (less than 0.1 nm), and similar for silicon and quartz (about 0.5 nm rms as deduced from AFM data), but all in the same range. Since the fractals are not present only on HOPG, we can safely hypothesize that it is not playing a role in determining the nanoparticle diffusion; (2) HOPG is conductive and the silicon we used for our experiments is doped (resistivity of few tens of ohm cm$^{-1}$) hence the nanoparticle can transfer their charge to both surfaces after landing. The main difference observed in the fractal morphology is in fact on the quartz surface, and we have provided a possible explanation of the long fractal chains observed in the online supplementary material (figure 6).

Finally we would like to discuss in more depth the important point of the size/mass dependence of cluster diffusion. The analysis of the diffusion mechanisms and the frictional properties of nanostructures on surfaces is a very active research field, known as nanotribology [30, 31]. In our simulations, each cluster diffuse with a probability which is independent from its mass or contact area. Such an assumption seems counterintuitive, since one might expect larger clusters to diffuse more slowly. The good agreement obtained with the experimental data, see (figure 5), using such assumption can have different explanations: either friction is finite but independent of the contact area and mass or it is very weak, almost zero (superlubricity). Even if the decrease of mobility with the increase of cluster size is a general trend for nanostructures [26, 30], deviations can occur when the cluster size increases [30] for several reasons. In particular it has been recently found [32] a strong increase of mobility as the thickness of the cluster increases and the cluster becomes three-dimensional, a phenomenon known as thickness-induced lubricity. A decrease of friction can also occur as substrate and slider have incommensurate lattices, leading to structural lubricity [31]. Most importantly it was found that the presence of contaminants, such as small hydrocarbon or water molecules, between the substrate and the slider, can lead to a friction coefficient which is independent of the contact area and mass [33, 34]. Also temperature can play an important role in reducing the friction. It is well known that the interaction between crystalline surfaces can lead to vanishing friction at temperatures close to the melting temperature [36]. Moreover in [35] it was noted that temperature acts as a lubricant, an effect called thermolubricity. In order to explain the fact that a size/mass independent diffusion is able to reproduce our experimental results so well, we suggest three possible main reasons which can lead to a diffusive coefficient which is weakly dependent or independent on the cluster size/mass: (i) our experiment is in ambient conditions, so the presence of contaminants can lead to a size/mass independent diffusion [33, 34]; (ii) our clusters are made of very hot nanoparticles. The high temperature of the clusters can greatly reduce friction, thus enhancing mobility [35, 36] and making diffusion weakly dependent on the cluster size; (iii) given that the diffusion of clusters is driven by thermal fluctuations, larger clusters will lose their energy slower than smaller clusters, thus compensating their smaller mobility.

Conclusions

We analyzed the formation of nanostructures obtained by fs-PLD of TiO$_2$ nanoparticles on different substrates at ambient conditions. In this paper we combined experimental and numerical results to show that the nanostructures are formed on the surface after landing by a diffusion mechanism. This point is shown in two steps:

(i) **Experimental evidence**: Under the same experimental conditions (laser fluence, distance of the substrate from the ablated target material, etc) very different structures are found on different substrates. While on HOPG we report the finding of single nanoparticles, on different substrates fractal aggregates of nanoparticles are found: fractal nanostructures on silicon, and hundreds of microns long fractal chains on quartz. This indicates that the relevant mechanism which leads to the formation of nanostructures occurs after the material has landed on the substrate. Indeed, if the aggregates were formed in flight and the role of the substrate would be negligible, we would find similar structures on the different substrates.

(ii) **Numerical evidence**: We developed a Monte Carlo model for fractal formation. Initially we assume that nanoparticles, with a size distribution taken from experimental data, are randomly distributed on a two-
dimensional surface. Thereafter we let the nanoparticles diffuse and aggregate, and we show that the fractal structures thus obtained are in qualitative and qualitative agreement with the fractal structures found experimentally. This fact strongly support the idea that the relevant mechanism leading to fractal aggregates is a diffusion mechanism occurring on the substrate after landing of the ablated material. The fractal formation mechanism proposed here is based on a minimal set of assumptions: size independent diffusion and irreversible aggregation of nanoparticles into larger clusters on the substrate surface. The Monte Carlo simulations reproduce very well the observed fractal structures, including their fractal dimension and their area distribution. Let us stress that often only the fractal dimension of nanostructures is addressed when comparing experimental data with numerical results. As shown in this article, the fractal dimension is not very sensitive to the specific mechanism of fractal formation. Thus, taking into account other observables, such as the area distribution of the fractals, is essential when comparing different models of fractal formation.

The success of a simple model of diffusion and aggregation to describe fractal structures in PLD experiments, where hot three-dimensional nanoparticles made of a large number of atoms land and diffuse on different substrates at RT and at ambient pressure, is highly non-trivial.

The results presented here are rationalized by taking into account the substrate thermal conductivity as major factor in determining the nanoparticle aggregation behavior. Hence our results may open new ways for several technological applications to engineer nanoparticle aggregates with tailored fractal dimension and area distribution.

Acknowledgments

GLC would like to thank F Borgonovi for useful discussion. We would like to thank E Gnecco for providing advices on nanoparticle lubricity. We also thank G G Giusteri, B Goncalves and P Jacobson for useful discussion and suggestions. This research has been partially funded by the Cariplo foundation grant on Controlled nanostructures by low-cost non-thermal laser ablation on metals at atmospheric pressure and by Università Cattolica del Sacro Cuore through D.2.2 grants.

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