Expansion-Limited Nanocluster Growth in a Plume Formed by MHz-Pulse-Rate Laser Ablation

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ABSTRACT

We study the formation of carbon nanoclusters created by MHz repetition rate - picosecond laser pulses. We show that the average size of a nanocluster is determined exclusively by single laser pulse parameters and is largely independent of the gas fill (He, Ar, Kr, Xe) and pressure, in a range from 20mTorr up to 200 Torr. We provide evidence of the formation of large clusters at higher pressures in excess of 400 Torr, where the gas fill density is comparable or higher to the density of carbons in the ablated plume, and use simple kinetic theory to estimate cluster sizes, which are in qualitative agreement with the experimental data. We conclude that at pressures well below 300 Torr, the role of the buffer gas is to induce a transition between thin solid film formation on the substrate and nanofoam formation by diffusing the clusters through the gas, with no significant effect upon the average cluster size. At the higher pressure the buffer gas serves as a confiner for the carbon plume, increasing the collision frequency between the carbon atoms and resulting in cluster size growth.

Keywords: laser ablation, carbon nanocluster

1 INTRODUCTION

Laser ablation has proven to be an efficient method for producing nanoclusters of different atomic content, shape and internal structure. Moreover, the size of a cluster has a significant affect upon various material properties and, therefore, provides a relatively simple experimental avenue to control those properties [1]. In this work we are, therefore, attempting to control the properties of carbon nanofoam via control over the size of carbon nanoclusters, which are the "building blocks" for this material. Carbon nanofoam shows the unique property of paramagnetic susceptibility of about 10-5 of that for transition metals, which is in striking contrast to the general diamagnetic behaviour of the carbon allotropes [2]. To create the nanofoam we have used the standard approach where a laser ablates a target in the presence of an inert ambient gas. The gas serves to confine the ablated atomic plume reducing its diffusion velocity and therefore retain the atoms at a temperature and density high enough for efficient atom-to-atom sticky collisions, resulting in cluster formation.

We report here experiments producing carbon nanoclusters that investigate the influence of gas fill type and pressure (including vacuum conditions), and laser fluence. From a simple kinetic approach it is possible to suggest that the effect of an ambient gas upon cluster size will not be seen until the gas pressure is increase such that the density is comparable to the density of atoms in the ablated plume. Also such an approach predicts the formation of clusters in vacuum conditions. In what follows we describe the experimental set-up, diagnostics, and results for cluster sizes in the different experimental conditions. We then present simple estimates of the average cluster size and compare them to our experimental data.

2 EXPERIMENTAL SETUP AND DIAGNOSTICS

Carbon nanofoams were made using a high power frequency doubled Nd:YVO_4 laser [3] operating at second harmonic (532 nm); repetition rate 1.5 MHz; pulse duration 12 ps; focal spot size as small ~ 15 microns; maximum incident intensity of $7x10^{11}$ W/cm^2 with corresponding fluence 8.6 J/cm^2. The fluence could be varied to below the ablation threshold by decreasing the energy per pulse using polarization optics. To avoid drilling of the target surface the laser was scanned using x-y scanning mirrors in a constant velocity (1ms^{-1}) spiral.

The foam was deposited upon copper TEM grids coated with holey carbon films (hole size 10-1000s of nm). Cluster size (cluster diameter) distributions (sample size ~ 500 clusters) were obtained via analysis of TEM images taken of various nanofoam samples. The distributions were then fitted with a Poissonian distribution fit to obtain an indication of the average size, and also analysed using statistical box and whisker plot methods.

3 EXPERIMENTAL RESULTS

Presented elsewhere [4], we conducted a series of experiments conducted to investigate the dependence of the cluster size upon various experimental parameters. These parameters included the laser scanning speed (0.1 to 1ms^{-1}), background argon pressure (2 to 200 Torr) and the type of filling gas (He, Ar, Xe, Kr at 50 Torr). This data showed that there is little if any significant difference in measured average cluster size (~ 4 ± 0.5nm) for the mentioned above experimental parameters. The sets of experimental results regarding argon pressure and background filling gas type

are important in that the lack of variance in cluster size indicates that there is little or no effect of the buffer gas upon the density of carbon in the cluster forming region. Combining this result with the result for cluster size at different scanning speed suggests that clusters form from the action of single pulses regardless of the presence of a buffer gas. Hence, it is necessary to investigate the appearance of deposited material at different pressures since the observations above imply that clusters should be found deposited upon substrates even in vacuum conditions.

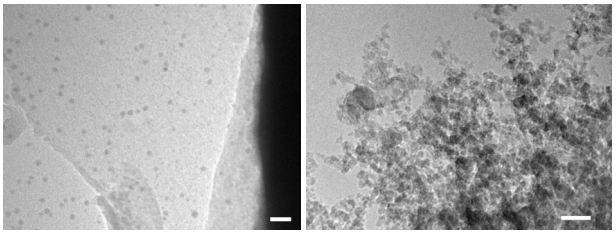

Figure 1. TEM images of carbon nanocluser material created in vacuum (left) and at 2 Torr (right). Both scale bars are 25 nm.

Figure 1 contains TEM images depicting the transitional nature of material deposition as pressure is increased from effectively vacuum, where mean free path is greater than the distance to the substrate, to 2 Torr. In vacuum conditions one generally produces diamond-like carbon films [5], however in our vacuum depositions clusters could be found on grids in shadowed areas where diamond-like carbon material was not deposited. The image on the left of figure 2 shows a region shadowed from the ablation source by the edge of a copper TEM grid where clusters were individually deposited on the holey carbon film.

As the pressure is increased from vacuum towards a few Torr, the presence of the background gas now serves to induce a transition between thin solid film formation on the substrate and foam formation, by diffusing the clusters through the gas. The resulting "web-like" can be seen in the right hand image of figure 1.

In addition to generating a cluster size distribution for clusters created vacuum, experiments were conducted to investigate the dependence of cluster size upon laser fluence. Nanofoam was therefore produced in an argon atmosphere of 50 Torr at fluences of 2, 4 and 8 J/cm^2.

Figure 2 contains box and whisker plots which depict the cluster size distributions measured for the three different fluences, in addition to a cluster size distribution generated from images of individual clusters found in shaded areas of vacuum deposited samples. There does not appear to be any strong dependence of cluster size upon fluence in this range. Also it is important to note the similarity of distributions for vacuum produced clusters to those produced at 50 Torr suggesting that there is little affect of the buffer gas at this pressure.

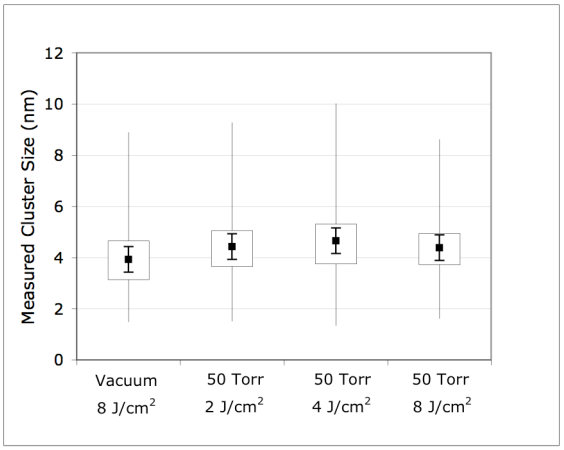

Figure 2. Box and whisker plots of cluster sizes of foam produced at various fluence compared to clusters produced in vacuum conditions. The data point with error bars is the numerical average size, which has an error of ± 0.5nm.

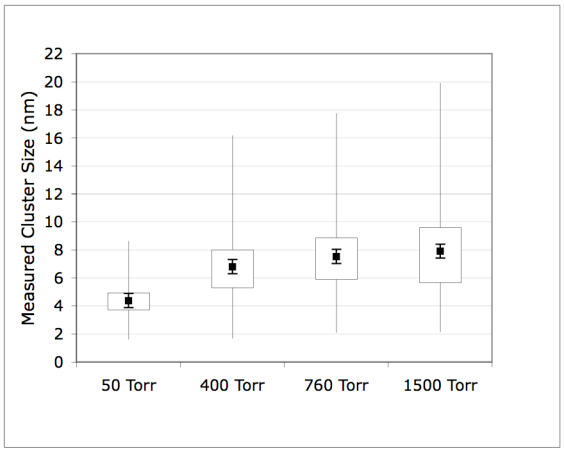

Figure 3. Box and whisker plots of cluster sizes of foam produced at various pressures. The data point with error bars is the numerical average size, which has an error of ± 0.5nm. The laser fluence is 8 J/cm^2.

Figure 3 represents the size distributions of clusters produced at pressures approaching and exceeding atmospheric pressure. Clearly there is a significant size increase for clusters produced at pressures greater than half of an atmosphere. At such pressures the density of carbons in the ablated plume, which is of the order 10^{19} cm^{-3}, is comparable to the number density of gas fill atoms. It is important to note that the average size of a cluster shows only a weak dependence with increasing pressure. For example, a four times increase in pressure from 400 to 1500 Torr produces and increase of the cluster size (diameter) from 6.8 to 7.9nm, much less than that predicted by simple kinetic theory [4]. We note however, that the maximum size increases much faster with the pressure raise.

This weak dependence can be accounted for by considering the ablation rate of carbon at different

pressures. Figure 4 shows that as the pressure is increased, ablation becomes less efficient due to factors such as laser scattering from the laser plume and buffer gas, and also re-deposition of material. As a result of a lowered ablation rate, the two competing factors of increased confinement and lower feedstock of ablated material to the cluster formation zone result in a reduced dependence of cluster size upon pressure.

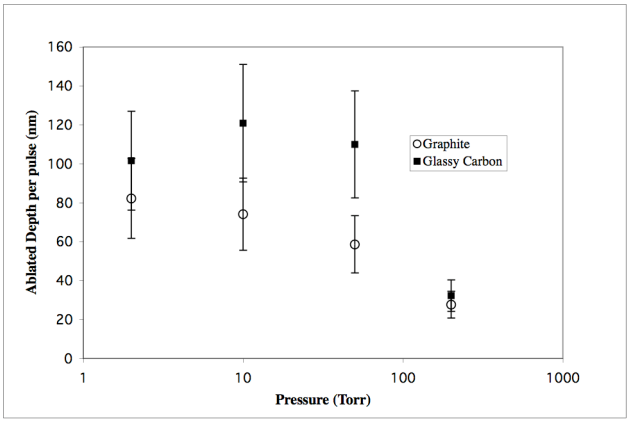

Figure 4. Measures ablation rate (grams/minute) for different pressures for graphite and glassy carbon targets at 1.5 MHz repetition rate.

4 CLUSTER SIZE CONSIDERATION

A simple model of cluster formation by a single pulse as a function of laser parameters has been presented elsewhere [4] and is summarized here. First, the flow of hot carbons is created during ablation. The laser pulse duration is too short for the clusters to be formed during the pulse. Therefore, after the end of the pulse the ablated vapours either diffuse, when the chamber is filled with a gas, or adiabatically expand into vacuum. The cluster formation process is considered as a consequence of atom-to-atom and atom-to-cluster sticky collisions under the assumption that the monomer addition process dominates nucleation.

4.1 Kinetics of cluster formation

On the basis of the previous studies of carbon nanotubes and carbon nanofoam formation [1, 6] one can suggest that the carbon clusters are created at a temperature higher than or close to T_{min}~ 1200 K. Let's take this temperature as a limit temperature for cluster formation in a plume: that is clusters cannot be formed if the temperature drops below this value. The expanding plume of ablated carbons cools down adiabatically either due to diffusion in the ambient gas or by expansion in vacuum. We define the time appropriate for cluster formation as a time when temperature in the plume is greater than the above limit. It follows [1, 6] that carbon-to-carbon and carbon-to-cluster sticky collisions (monomer addition) play a major role in cluster formation. Moreover, the carbon-to-carbon collision time is an appropriate scaling time for estimation of the maximum number of carbons, which can stick together. We estimate the maximum number of carbons that could be attached together as a ratio of the time when temperature is above the appropriate minimum, to the time of carbon-carbon collision.

4.2 Carbon cluster formation in ambient gas

Taking the above suggestion that the formation time, t_{min}, for clusters is governed by the fact that the average temperature in the plume must be greater than ~1200K, it is possible to show [4]:

$$t_{\min} = \frac{3n_{ar}\sigma}{v_{carb}} \cdot \left(l_{abl}\right)^2 \cdot \left(\frac{T_0}{T_{\min}}\right)^{2/(\gamma-1)} . \qquad (1)$$

Here n_{ar}, σ *and* v_{carb} are the argon number density, collision cross section and carbon velocity respectively; l_{abl} is the ablation length and T_0 is the initial temperature of the ablated plume. Taking n_{ar} ~3x10^{18}cm^3; σ ~ 10^{-15} cm^2; v_{carb} ~ 10^6 cms^{-1}; l_{abl} ~ 50nm and T_0 ~ 25eV (γ=5/3) one obtains t_{min}~10^{-6}s. We make the approximation that the carbon-to-carbon collision time is an appropriate representation of the sticky collisions (t_{coll} ~ t_{sticky}) where the time for such collisions at carbon density n_c in volume V_1 reads:

$$t_{sticky} = \left(n_c \sigma_{att} v_c\right)^{-1} = \frac{V_1}{V_0}\frac{1}{n_0 \sigma_{att} v_c} = \frac{1}{n_0 \sigma_{att} v_c}\left(\frac{T_0}{T_{\min}}\right)^{1/(\gamma-1)} \qquad (2)$$

and includes the attachment cross section σ_{att}, and the volume, V_1 defined by plume expansion in the time t_{min}. Note that the attachment cross section is unknown, and it is definitely lower than elastic cross section taken for diffusion above. The maximum number of carbons that can be combined together to form a cluster with the experimental parameters used is estimated as follows

$$N_{\max} \approx {t_{\min}}/{t_{sticky}} = 3n_0 \cdot n_{ar} \cdot \sigma \cdot \sigma_{att} l_{abl}^2 \left(T_0/T_{\min}\right)^{3/2} \qquad (3)$$

$$r_{cluster} = \left(N_{\max}/\left(4\pi n_0/3\right)\right)^{1/3} . \qquad (4)$$

At 50 Torr one obtains N_{max} < 7x10^4 corresponding to a cluster radius ~ 5.3 nm: while at 1500 Torr $r_{cluster}$ ~ 15 nm, in qualitative agreement with experimental results. Hence we present a qualitative understanding of the cluster formation process whereby clusters form in three distinct regimes, those being low, moderate and high pressure. Low pressure corresponds to the situation where cluster size is not affected by gas pressure in the ablation plume at $n_{ar} << n_c$. In the moderate pressure regime (~100 to 400 Torr, $n_{ar} \leq n_c$), clusters form according to the kinetic expressions given above (Eqs. 1-4) and cluster size increases with increased pressure. Finally, in the high-pressure regime, $n_{ar} \geq n_c$, there is no significant dependence

of size upon pressure. This is due to competing effects of the buffer gas at the elevated pressure. First, the gas serves to reduce diffusion and hence increase confinement. Due to the high concentration of Ar atoms in the formation region, the time for sticky collisions is increased since carbon-argon collisions are more frequent at higher pressure. This acts as increasing the cluster size. In opposition to this is a reduction in the formation time via reduced ablation length l_{abl} and coefficient of absorption A (Eq. 1,3). This is observed via significant drop in the ablation efficiency at higher pressure (see figure 4). As a result, the size of a cluster saturates at a pressure around 1 atm.

4.3 Clusters formed by single pulse in vacuum

Carbon clusters can be formed in an adiabatically expanding plume in vacuum until the temperature drops to the minimum temperature for cluster formation, T_{min}. In the one-dimensional expansion case one easily obtains the plume volume as $V_1 = S_{foc} t_{\min} v_{carbon}$, and maximum time allowed for the cluster formation as $t_{\min} = V_1 (s_{foc} v_{carbon})$. Taking $t_{sticky} = V_1 / (V_0 n_0 \sigma_{att} v_c)$ the maximum number of atoms per cluster with the sticky collision time taken in accordance to (2) is as follows:

$$N_{\max} \approx t_{\min} / t_{sticky} = n_0 \cdot \sigma_{att} \cdot l_{abl} \qquad (5)$$

In the experimental conditions of this paper the above formulae gives N_{max}~500 atoms and $r_{cluster}$~1 nm, which is in qualitative agreement with the experimental data. We note that the average carbon density in the formation zone comprises n_c~ 3.37x10^{19} cm^{-3}, which is comparable to the number density at atmospheric pressure. This is the reason why carbon clusters form during a single pulse and in vacuum. However, this density is an underestimate for the carbon density for cluster formation as the spatial density distribution in adiabatic expansion is steep, and the contribution of higher density areas into formation process should be significant. We will consider this problem elsewhere.

5 DISCUSSION AND CONCLUSIONS

The salient feature of our findings that has not been uncovered to date to the best of our knowledge is an independence of the cluster size on the conditions in the formation chamber: Change of the gas (He, Ar, Kr, Xe) and change of the gas pressure in a range from 20 mTorr to 200 Torr does not affect the average cluster diameter that was found to be 4±0.5 nm. In the experiments the number density of carbon in the plume is approximately 3.5×1019 atoms/cm3, which is comparable to that of atmospheric pressure. Therefore in all of the low-pressure (≤ 50Torr) experiments, the effects of confinement of the ablation plume due to the background gas are weak because $n_{carbon} >> n_{gas}$. Here, the role of the gas becomes the prevention of film formation on the substrate instead producing the "web-like" foam structure.

In addition to promoting the formation of the foam structure of the material, the presence of a buffer gas at high pressures promotes the cluster formation process by increasing the number density of carbons available in the formation region such that larger clusters can be produced. Clusters of average size 8 ± 0.5nm were produced at 1500 Torr compared to clusters of 4.4 ± 0.5nm at 50 Torr. Also the effect of increased pressure in reducing the ablation rate is noted as the reason for weak dependence of cluster size upon pressure in the high-pressure regime.

The simple model used above underestimates the cluster size in vacuum for carbon clusters because it ignores the steep spatial density distribution during the adiabatic expansion. We will present the model with this effect taken into account elsewhere. However, the replacement of constant density by a two-step distribution already results in doubling of the average cluster size.

To conclude we found that a single laser pulse can form carbon nanoclusters in vacuum, with well-defined size, even with high-repetition-rate laser pulses where the time gap between the pulses is as small as 660 ns. Also we found that in a broad parameter range it is possible to observe dependencies of cluster size upon experimental parameters. This is exemplified by measurement of large clusters produced at pressures above 400 Torr. It is clear that there is a strong opposing interplay between experimental parameters such as laser fluence and pressure, which strongly affects cluster formation. It is worth mention that there is a possible interaction between proceeding laser pulses and already-formed nanoclusters in the plume, which may affect cluster size. We will investigate this possibility in the near future.

ACKNOWLEGDEMENTS

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