Plume diagnostics and room-temperature deposition of carbon nanotubes and nano-onions at 248 nm

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Abstract. We report on the deposition of carbon nanotubes and nano-onions at room temperature using excimer laser radiation at 248 nm to ablate mixed graphite-nickel/cobalt targets in the presence of O$_2$ gas. The carbon nanotubes are frequently seen to connect individual onions and have a wall thickness on the order of 20-25 nm, with an overall external tube diameter of 100-200 nm. These tubes have notably large channel diameters and are significantly larger than typically reported single and multi-walled carbon nanotubes. The observed onion structures are both single and clustered and are 100-200 nm in diameter. Ablation of the same targets in comparable pressures of Ar does not result in these nanostructures but instead produces amorphous carbon. Ablating a pure graphite target under the same laser conditions, with or without metal, also does not yield the tubes and onions. In-situ time-resolved emission spectroscopy has been used to follow the emission from molecular carbon such as C$_2$, as well as metals such as Ni or Co in the different ambients.

1. Introduction

There has been a tremendous interest in carbon nanoparticles since the discovery of the carbon nanotube in a high-temperature arc [1]. While laser ablation methods for carbon nanotubes have predominantly employed the Nd:YAG laser for ablation, [2-4], there are also a few reports on the use of excimer laser radiation [5,6]. In all cases the depositions have involved a high-temperature furnace (typically at 1200°C) or a heated substrate (500-1100°C), and several hundred Torr of Ar pressure. Carbon nano-onions are another class of interesting nanostructures [7-9]. They were first revealed as concentric shell structures, 3-7 nm in diameter, observed during the evaporation of carbon by arc discharge in vacuum [7]. The size of the innermost shell (0.8 – 1.0 nm) was very close to that proposed for the fullerene carbon cluster [7].

To the best of our knowledge there are no reports in the literature for room-temperature carbon nanostructure formation using excimer lasers. Here we report on the deposition of nanotube structures with large, 100-200 nm external diameters and graphitic carbon nano-onions at room temperature in an ambient of O$_2$ by the pulsed laser ablation of a Ni-doped or Ni-Co-doped graphite target at 248 nm. The generation of such structures shows a complex dependence on the composition of the target. Time-resolved emission spectroscopy was employed to identify components of the plume under various conditions to correlate the carbon deposits with the plume chemistry.

2. Experimental

For our laser ablation experiments commercially available pure graphite targets and composite Ni and Ni-Co doped graphite targets were used. The graphite-metal targets were prepared by pressing a
mixture of graphite powder (Alfa Aesar) and graphite cement (Dylon Industries Inc.) in a 1:1 wt. ratio, with 1 at. % of Ni or 0.5 at. % each of Ni and Co powders (Alfa Aesar), at 15 KPsi, at 130 °C for 4 h. This was followed by annealing in flowing Ar at 450°C for 8 h.

The targets were irradiated with a KrF laser (248 nm, 25 ns FWHM, and laser intensity of $8 \times 10^8$ W/cm$^2$). The pressures (2 Torr) of O$_2$ and Ar gases were controlled with a needle valve. Ablation products were deposited onto Si substrates. Transmission electron microscopy (TEM) was performed with a Hitachi H-9000 electron microscope, at 300 KV. The best TEM samples were prepared by wiping a holey carbon grid across the Si substrate. Emission spectra of species in the plume were measured using two gateable (4 ns), intensified CCDs, each mounted on the exit ports of a 0.3 m spectrometer equipped with appropriate gratings (300 gr/mm blazed at 500 nm, 600 gr/mm blazed at 300 nm, and 2400 gr/mm holographic grating blazed at 250 nm).

3. Results and Discussion

3.1. Characterization of Deposits by Ablation

The carbonaceous material that was deposited during ablation showed a complex dependence on the target composition as well as the buffer gas employed. In addition, we have observed differences due to the metal catalyst added to the target. A pure graphite target yields amorphous carbon with both O$_2$ and Ar. When ablating in O$_2$, only a thin layer of amorphous carbon is deposited. In the presence of Ar, loosely packed and sooty material is deposited very rapidly. Featureless selected area electron diffraction (SAED) patterns are seen in the TEM images in both cases, indicating that the material is amorphous.

A graphite target comprising 1 at.% of Ni or 0.5% of both Ni and Co, when ablated under the same conditions, yields very different results depending on the buffer gas. Similar to graphite, the ablation in Ar yields a dense, sooty deposit, which is amorphous as determined by TEM. However, when ablating in O$_2$, both carbon nanotubes and onion-like graphitic nanostructures are obtained. These structures are described below.

TEM images of carbon nanotubes Fig. 1(a,b) and nano-onions (Fig. 1c) are shown below. The tubes have a wall thickness on the order of 20-25 nm, with an overall external diameter of 100-200 nm. Tube lengths vary from 1.0 μm to 3.5 μm. These tubes are significantly larger than typically reported single and multi-walled carbon nanotubes, and have notably large channel diameters. In some tubes, metal particles can be observed both at the end of the tube (Fig. 1a) as well as filling sections in the middle. Dark field TEM imaging off the (002) graphitic reflection (Fig. 1b) established that the tubes were hollow.

Fig. 1 (a) TEM images of carbon nanostructures produced at room temperature by excimer laser ablation in 2 Torr O$_2$; (a) nanotube with metal at tip, (b) dark field TEM image of tube showing graphitic walls and hollow tube, and (c) individual and clustered nano-onions.
SAED performed on these tubes shows a combination of arcs that match the (002) graphite d-spacings (3.37 Å) and bright dots (2.02 Å and 1.75 Å), which correlate to Ni and Co lattice spacings.

The nano-onion structures (Fig. 1c) are both individual and clustered and have diameters of 100-200 nm, with observable strands that are 5-10 nm wide. These structures are larger than the nano-onions reported in the literature and are not as perfectly spherical. The lattice spacing from structures in 3 different samples was measured with high-resolution TEM and was found to be 0.340 ± 0.005 nm, which corresponds to the (002) lattice planes in graphite. Structures that are observed in the TEM range from tightly wound and spherical to more extended and disorganized with open spaces. At first glance the TEM images appear to resemble filaments that are wound up. We have not yet established if these structures are in fact filaments or are crumpled sheets that give a perception of filaments in a TEM image.

3.2. Spectroscopy of the Plume
Reference spectra were taken by ablating a pure graphite target in high vacuum (10⁻⁸ Torr) as well as in the presence of 2 Torr of Ar and O₂, respectively. Characteristic Swan band emissions from the C₂ molecule are observed. These are due to vibrational transitions between the excited and ground electronic states d ¹Π₉ → a ¹Π₆, with band heads at 463.5 nm (Δv = 1), 516.5 nm (Δv = 0), and 550.5 nm (Δv = -1), respectively [10]. In vacuum, the Swan band emission can be observed at delays starting at 600 ns and is detectable to about 7 μs. In both Ar and O₂, the Swan bands are extremely intense and can be detected for up to 40 μs when using a 1 μs gate.

With the graphite-Ni-Co target, emission intensity from C₂ is significantly enhanced both in O₂ and Ar. In O₂, (Fig 2a) C₂ emission is again detected for up to 40 μs, although it is weak after 20 μs. In Ar, the C₂ emission can be detected to nearly 100 μs, especially from the (0-0) band head, although at delays of 40 μs and longer, additional peaks are also seen in the spectra (not shown here).

In both Ar and O₂, very long-lived atomic emission from the metals is observed starting at a delay of 500 ns. A typical Ni I - Co I spectrum, as shown in Fig. 2b, has a shoulder at 339.6 nm, and lines at 342.6 nm, 348.7 nm, and 353.1 nm. Two additional lines are present at 358.3 nm and 362.8 nm. These lines overlap with individual Ni I and Co I lines [11]. In O₂, the Ni I – Co I emission can be detected to 40-50 μs delays, while in Ar this emission is detected even at 400-500 μs.

Our observation of long-lived C₂ is similar to results reported at 1000 °C [12]. Since the radiative lifetime of the C₂ in its d ¹Π₉ state is only 185 ns [13], there must be a mechanism by which C₂ is continually generated in its excited state. Arepalli et. al [14] suggested that C₆₀ can generate C₂ directly by photodissociation and/or by a series of chain reactions involving daughter fullerenes. This or other mechanisms of sustaining C₂ in its excited state are needed to explain why we observe C₂ emission for several microseconds. Formation of carbon clusters / fullerenes in the plume could also explain the formation of the onion structures we observe. Atomic emissions from Ni and Co are
detected for long periods close to the target surface, hence the formation of large metal clusters must occur at longer distances from the target as the plume expands and cools into a room temperature background, followed by graphitization around these large metal clusters.

Carbon nanotubes generated by room-temperature excimer laser ablation differ from those grown at high temperatures in that (a) they are not single-walled nanotubes (SWNTs), (b) they have significantly larger external tube diameters (100-200 nm), in contrast to 1-2 nm for laser ablated single-walled nanotubes and 10-40 nm for the multiwalled nanotubes, and (c) they have a gnarled, bamboo-like structure rather than walls that are perfectly parallel to the tube axis, as well as having tube diameters that vary. Also, most of the tubes do not have metal fillings; a few have metal at the tip and/or in the central portion of the tube. Our onion structures resemble onions previously reported [7-9], but have significantly larger diameters of 100-200 nm. The formation of the nanotubes and nano-onions both occur in an O\textsubscript{2} ambient, strongly suggesting reactive pathways that involve O\textsubscript{2}. Additional experiments are in progress to determine the exact role of O\textsubscript{2} in forming these carbon nanostructures.

4. Conclusions
Excimer laser ablation of Ni and Ni-Co-doped graphite targets at 248 nm and at room temperature, in the presence of O\textsubscript{2}, produces carbon nanotubes and carbon nano-onions with large diameters on the order of 100-200 nm. Such structures are not observed when ablating the same target in Ar at the same pressures, instead amorphous carbon is produced, which indicates that O\textsubscript{2} initiates a reactive pathway essential for the formation of these structures. We also do not observe such structures when ablating a pure graphite target in O\textsubscript{2} or Ar. Time-resolved emission spectroscopy has been used to identify components in the plume. Under high fluence conditions, atomic Ni I / Co I, C I, and ionic C II species are observed. In addition, intense emission from Swan bands of the C\textsubscript{2} molecule is seen both in O\textsubscript{2} and Ar. The emissions from C\textsubscript{2} and Ni I / Co I are detected significantly longer in Ar atmospheres than in O\textsubscript{2}.

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