Gamma Radiation Effects in Vertically Aligned Carbon Nanotubes

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Abstract—This paper describes an experimental study of gamma radiation effects in low-density arrays of vertically aligned carbon nanotubes. These arrays are characterized by excellent anti-reflective and absorbing properties for wavelengths from UV to IR which makes them an interesting option for stray light control in optical space applications. Gamma irradiation equivalent to an estimated surface life-time exposition in geostationary orbit does not affect the reflectivity of the structures. First high-energy proton irradiation studies indicate that the reflectivity of the carbon nanotubes forests remains unchanged.

Index Terms—Carbon nanotubes, gamma-ray effects, radiation effects.

I. INTRODUCTION

Carbon nanotubes (CNTs) are among the most intensively studied materials and are currently in the focus of the nanotechnology research [1]. One of the forms of CNTs are vertically aligned carbon nanotubes (VA-CNTs), synthesized perpendicular to the substrate and referred to as CNT forests or CNT carpets. Recently, an ideal black material has been reported formed by a low-density array of VA-CNTs [2]. The experimental results presented in [2] make this carbon derivative medium the darkest man-made material ever, probably darker than any naturally occurring material on earth [3]. VA-CNT forests can absorb light almost perfectly across a very wide spectral range covering 0.2 – 200 µm [4].

VA-CNT arrays have the potential to provide order-of-magnitude improvement over current black paints and surface treatments and are considered as an interesting option for stray light control in optical space applications [5]. One of the challenges in space is the presence of cosmic radiation, especially for components directly facing to space. The most important radiation effect observed in CNTs is the displacement of atoms from their structure [6], leading to a multitude of consequences such as nanotubes bending, creation of links between nanotubes, or welding of crossing pristine tubes [7].

Even though the environment in space is dominated by protons and electrons [8], it is common to simulate the radiation in space with gamma sources. Proton and electron irradiations demand large accelerator facilities, whereas gamma sources are typically more readily available. The threshold energy of carbon displacement in CNTs corresponds to electrons with an energy of 100 keV [6]. The secondary electrons produced in Compton interactions and by ionization due to the primary 60Co photons carry enough energy (1.2 MeV) to induce observable displacement damage effects. Structural changes induced by 60Co photons reported in the literature include: nanotube shortening; decrease of nanotube diameter; structural instabilities; and/or change of interlayer spacing [9]–[12].

While the effects of electron or ion irradiation of CNTs have been intensively investigated [13] and led even to irradiation engineering of various CNT nanostructures [7], [14], to the best of our knowledge there are no results that have been reported on the radiation effects in vertically aligned CNTs. The aim of this work is to investigate the influence of gamma radiation on the optical properties of VA-CNTs in view of the space qualification of such absorbing layers.

II. SAMPLE SYNTHESIS

Multi-walled VA-CNTs were synthesized on a Si wafer substrate by chemical vapour deposition (CVD) using ethylene as the carbon source and a mixture of argon and hydrogen as the carrier gas. The substrate temperature and the process pressure for CNT growth were 973 K and 0.1 bar, respectively [15]. The CNT length was increased by addition of 100 ppm water vapour. A scanning electron microscope (SEM) image of the fabricated sample is shown in Fig. 1. The manufactured nanotubes are characterized by the diameter of 7 – 10 nm. The length of CNTs is either 11 µm or 80 µm and the density of the forest is 9 · 10¹⁰ CNTs/cm².

It should be noted that the geometry of the VA-CNTs used in this study is not optimized for ultra-low reflection in the visible spectral range. The extremely dark material based on VA-CNTs and reported in [2] is characterized by the nanotube diameter of 8 – 11 nm, CNT length of 300 µm and density of 7 · 10¹⁰ CNTs/cm². However, the irradiation effects investigated in this study are expected to be representative for all kinds of VA-CNTs forests and these results will guide the future selection of samples in order to better understand the radiation effects in such materials.

III. EXPERIMENTS

Gamma irradiation of the samples was carried out at the GammaMat TK1000A facility of Fraunhofer INT at room temperature in air. The point-like source allows the variation of the dose rate by varying the distance between the source and the sample. Dosimetry was done with calibrated ionisation chambers from which a numerical model was derived that described the dose rate around the source as a function of the sample geometry, distance and time.
Fig. 1. VA-CNT forest of 11 µm thickness synthesized on a Si substrate.

The CNT samples were placed above the irradiation source (Fig. 2) with several milimeters of a dose-buildup layer. The radioactive pellet is placed inside the guiding tube (seen as the stainless steel rod in Fig. 2). The position of the activated source is indicated with a thin rim just below the leftmost sample. To investigate the dose dependence, four 11 µm long VA-CNTs samples were irradiated for two weeks up to total doses of 0.5, 1.2, 4.6, and 11.7 MGy, respectively. In parallel, another sample of 80 µm long VA-CNTs was irradiated up to 11.7 MGy. The dose range of several MGy might be expected in geostationary orbit in 10-15 years of exposition time on the surface of a satellite [16].

Three investigation methods were used to detect the possible effects of the radiation in the samples. SEM images of the samples were taken before and after irradiation to identify potential structural changes of the VA-CNTs. Raman spectroscopy was carried out to yield information about the quality and disorder effects in the samples. Since the proposed applications utilize the unique optical properties of VA-CNTs the reflectance was measured before and after gamma irradiation.

Raman spectra were obtained in the 100 – 3000 cm⁻¹ regime using a Horiba Jobin Yvon LabRam spectrometer. The laser excitation wavelength was 785 nm.

The optical experimental setup is shown in Fig. 3. The total reflectance of the CNT forest was measured using an integrating sphere with the diameter of 25 cm. The CNT sample was placed on the sample holder at the center of the sphere. A silicon detector measured both the specular reflection (in the detector direction) and diffuse reflection (scattered into the entire hemisphere) [17]. A green laser diode module (532 nm) characterized by a beam spot diameter of 1 mm was used as the light source.

The irradiated samples, i.e. the four 11 µm long VA-CNTs characterized by doses between 0.5 and 11.7 MGy and the 80 µm long VA-CNTs with a total dose of 11.7 MGy were investigated with the SEM and the Raman spectrometer. The last sample, the CNT forest of 80 µm thickness, was additionally characterized by the measurements of its optical properties.

IV. RESULTS

A. SEM images

The inspection of SEM pictures did not reveal any severe structural damages in the irradiated VA-CNT forests - the nanotubes seemed to be intact. However, the thorough investigation of the top surface of the CNT forest uncovered slight changes in the structure even for the lowest dose of 0.5 MGy. The nanotubes were shortened in length by few µm whereas the CNT tip endings were thicker which influenced the tip bending (Fig. 4). For the pristine sample the measured diameter of the CNTs in their tip region was about 25 nm, whereas for the irradiated one it was approx. 35 nm. The length of the thicker part of the nanotubes’ tip endings increased from 120 – 160 nm for the pristine sample to 200 – 275 nm for the irradiated ones. This is in agreement with numerical models that indicate a higher damage sensitivity of the CNTs endings compared to the bulk part [18].
The thicker part of the pristine VA-CNTs tip endings revealed from SEM images results from impurities in the fabrication process. The gamma irradiation, however, enhanced this effect by introduction of defects and resulted in slightly changed overall surface corrugation. Since the random surface profile is one of the key factors that make the VA-CNTs absorber an ideal black object [2], one might expect a degradation of the optical (anti-reflective) properties of the irradiated samples.

C. Raman Spectrometry

Raman spectra of 11 µm long CNTs before and after irradiation are shown in Fig. 5. The major features observed in this figure are the D and G peaks around 1340 cm$^{-1}$ and 1550–1600 cm$^{-1}$, respectively [19]. The D-band is a measure of disorder in graphitic materials and may be attributed to defects in the curved graphene sheets and tube ends, whereas the G-band corresponds to the tangential vibrations of the carbon atoms and is a measure of the graphitization of the sample [12], [19].

To assess the quality of a CNT sample, one typically investigates the intensity ratio of the D-peak and the G-peak. The corresponding $I_D/I_G$ values for the samples before and after irradiation are given in Fig. 5. Comparison of $I_D/I_G$ factors leads to the conclusion that there are no significant changes in the properties of 11 µm long VA-CNTs due to the gamma irradiation. For longer 80 µm nanotubes gamma irradiation leads to a small increase of the $I_D/I_G$ factor that indicates a growing number of defects in VA-CNTs (Raman spectra shown in Fig. 6). The deviation of the $I_D/I_G$ ratios obtained for the 11 µm and 80 µm irradiated CNTs corresponds to the larger interaction length of the gamma radiation with the nanotubes for the thicker sample. More exposed material yields a higher sensitivity to radiation-induced changes that is reflected in the measured Raman spectra characteristics.

It should be noted that the number of defects in pristine VA-CNTs related to the quality of the samples is relatively high and may influence the sensitivity of the $I_D/I_G$ observations (the ratio of intensities of the D and G bands does not change

### Table I

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Initial Meas.</th>
<th>2nd Meas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>81 % (pristine)</td>
<td>78 % (pristine)</td>
</tr>
<tr>
<td>Polyester</td>
<td>3 % (pristine)</td>
<td>4 % (pristine)</td>
</tr>
<tr>
<td>VA-CNTs</td>
<td>0.7 % (pristine)</td>
<td>0.5 % (irradiated)</td>
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the low density of CNTs and their finite length, the energy deposited in the material is relatively low. Extrapolating the data given in [21] yields a stopping power of about 5 eV/nm.

The reflectivity and Raman spectra have been measured before and after proton irradiation. The reflectivity of the sample remained at the level of 0.5%. The Raman spectra did not reveal any degradation that could be attributed to structural damages in the sample.

Since this irradiation was done parasitic the fluences were low compared to other studies of proton irradiations [22], [23] in which massive changes in the structural integrity of CNTs were observed for more than $10^{18}$ protons/cm$^2$.

VI. CONCLUSION AND OUTLOOK

Gamma radiation dosis equivalent to 10-15 years of surface exposition time in geostationary orbit does not lead to apparent structural damage of vertically aligned carbon nanotubes. The most important optical parameter for this application, reflectivity, is not affected by the gamma irradiation making VA-CNTs an interesting candidate for space applications.

The ongoing work will focus on two aspects: The VA-CNTs samples used for this study were not optimized for anti-reflective optical applications and might be therefore less sensitive to radiation than optimized geometries. Secondly, the absorber coatings based on VA-CNTs could be potentially used on surfaces directly exposed to space and hit mainly by low energy particles that deposit their energy completely in the sensitive structure. This requires further studies of irradiation effects caused by high fluences of low-energy protons.

Future study will enable us to assess the trade-off between the positive effects of longer VA-CNTs regarding their optical properties and the negative effects related to the possible higher radiation sensitivity of longer nanotubes.
REFERENCES


