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J. Kuhnhenn

V. Khavrus

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Proton radiation effects on the optical properties of vertically aligned carbon nanotubes

J. Kuhnhenn, G. Lubkowski,
Fraunhofer INT
Euskirchen, Germany

V. Khavrus, A. Leonhardt
IFW Dresden
Dresden, Germany

D. Eversheim, C. Noll,
S. Hinderlich, A. Dahl
HISKP University Bonn
Bonn, Germany

***Abstract*—This paper discusses proton-induced radiation effects in vertically aligned carbon nanotubes (VA-CNT). VA-CNTs exhibit extremely low optical reflectivity which makes them interesting candidates for use in spacecraft stray light suppression. Investigating their behavior in space environment is a precondition for the implementation on a satellite.**

***Index Terms*—Carbon nanotube, stray light, radiation effects, proton irradiation, VA-CNT**

I. INTRODUCTION

Several optical applications demand extremely low reflective materials for stray light or noise reduction. In 2008 Yang et al. presented an experimental observation of an extremely dark material made by a low-density nanotube array [1], which was theoretically predicted in 1997 [2]. Shortly after that the potential use for space applications came into the focus of researchers [3][4]. The vertically aligned carbon nanotubes (VA-CNT) demonstrate a high absorption that was measured to be angular independent for the light of wavelengths between 200 nm and 2 µm [5]. Such result originates from the sophisticated configuration of the VA-CNTs; however, their structural stability in a space environment has to be investigated. It was already shown that vacuum and temperature variations have no negative influence on the structure of VA-CNTs [6]. On the other hand different carbon nanostructures exhibited significant modifications under radiation [7]. However, no publication discussed the possible influence of radiation on the optical properties of VA-CNTs until recently, when we showed that gamma radiation did not change the reflectivity of VA-CNTs even after a dose of more than 10 MGy [8].

If the surface of the VA-CNTs is exposed directly to space without any shielding, another major damage process to be expected is the displacement of atoms induced by the high fluence of low energy protons. Investigation of the radiation sensitivity is the prerequisite for a potential implementation of this technology in future space applications.

In this paper we present for the first time results about the influence of low energy proton irradiation on the optical properties of highly absorbing VA-CNTs.

II. EXPERIMENTAL

A. Sample preparation

Multiwalled VA-CNTs were synthesized on a Si-wafer substrate by aerosol-assisted (samples Ae_54/B-6, Ae_58/A-6, and Ae_62/A-8) [9] and low-pressure (sample LP447a) chemical vapor deposition. The carbon nanotubes are characterized by a diameter of 7-10 nm and a length of 500-2500 µm. The samples were 10×20 mm². Three of the samples (Ae…) exhibit a higher reflectivity (around 3%) compared to the fourth (LP447a) because a different catalyst system was used. The difference is the residual position of the metal catalyst on the top of the VA-CNTs or at the bottom, respectively. The metal particles at the ends lead to a higher reflectance.

B. Irradiation

The irradiation was done at the isotope separator facility at the University of Bonn [10]. This accelerator (see Fig. 1) is able to deliver protons with energies between 1 keV and 160 keV with currents up to 10 µA.

The proton energy for the irradiation was chosen to make sure that the whole energy was deposited in the VA-CNT. The stopping power of the protons reaches a maximum around

Fig. 1 The isotope separator at the University Bonn used for proton irradiation. The samples were placed in a vacuum chamber.

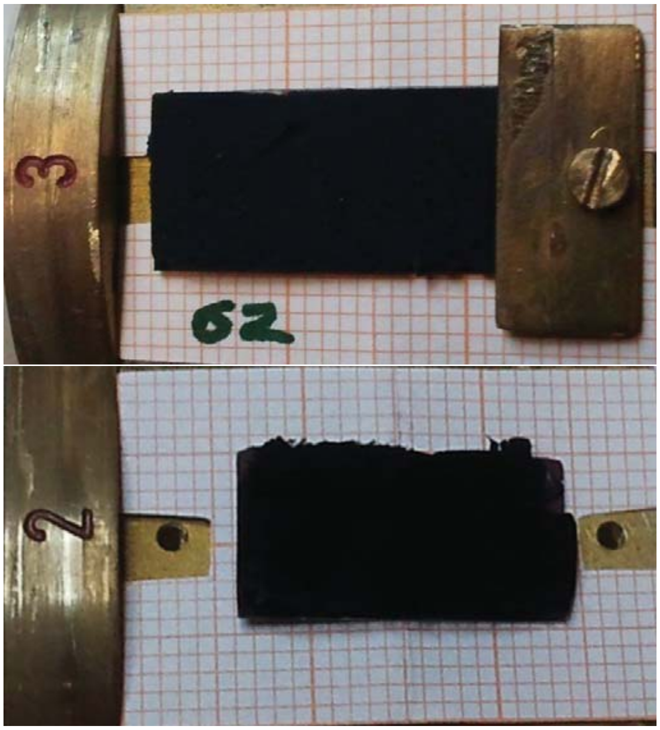

Fig. 2 Two of the samples (top: Ae_62/A-8, bottom: LP447a) before irradiation.

100 keV [11]. In total 4 samples were irradiated with fluences of 10^{15} p/cm², 10^{16} p/cm², 10^{17} p/cm², and 5×10^{17} p/cm² in vacuum with a proton energy of 80 keV (see Fig. 2). The proton currents varied between 3.3 µA and 9.2 µA. The fluence of 5×10^{17} p/cm² corresponds to the estimated maximum proton fluence expected in 15 years geostationary orbit without shielding.

C. Reflectivity measurement

The optical reflectivity of the VA-CNTs is measured at 532 nm in an integrating sphere as shown in Fig. 3 . The laser light is focused on the sample with a spot size of 100 µm. The optical design of the laser makes sure that 99.9% of the emitted light is focused onto the sample.

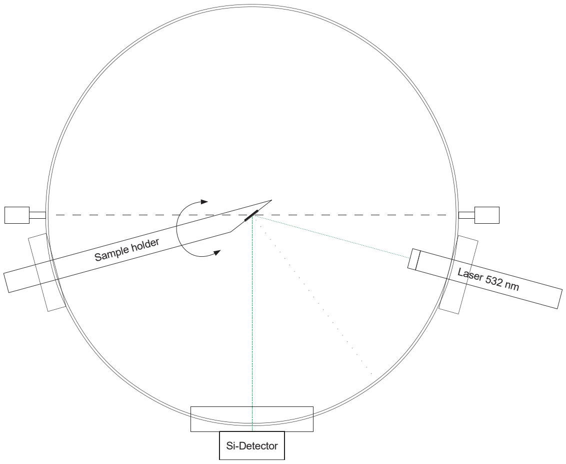

Fig. 3 Measurement of total reflectivity of VA-CNTs samples using an integrating sphere. The samples can be rotated on their sample holder to measure both direct and indirect reflection.

The sample is placed on the sample holder to measure either in direct reflection or in a rotated position where direct and scattered portion of the incident light is measured.

The optical power is measured with a HP 81520A optical head connected to a HP 81533B sensor unit in a HP8163A mainframe. Measureable light powers range from -100 dBm up to 10 dBm. The background signal with the laser turned off is below -90 dBm. The signal from the laser without a sample gives -29.6 dBm in indirect configuration.

Using white paper as a control sample yields a total reflectivity of 78%. This corresponds to change of optical power of 1.1 dB. The measurements repeated several times for each sample yielded an uncertainty of 0.5 dB.

D. Electron microscope images

Additionally the VA-CNTs samples were characterized with an electron microscope before and after irradiation. The images are taken in side view for which the samples are broken along a defined axis to make sure that the irradiated area is crossed.

III. RESULTS

A. Visual inspection

The samples showed no detectable change from visual inspection. In contrast to that the high energies deposited by the proton beam is clearly visible in the paper below the samples that is used to adjust the samples to the beam (Fig. 4).

After several days a very small effect could be observed in

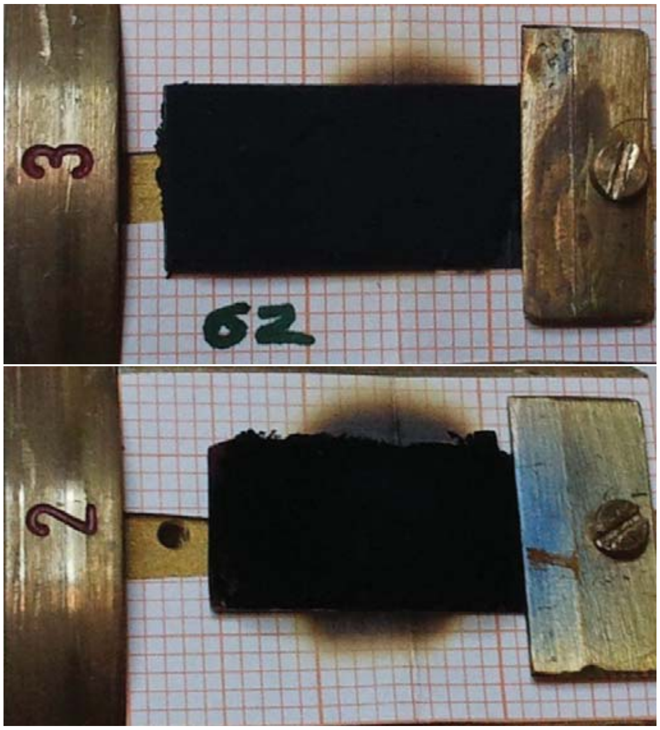

Fig. 4 Two of the samples (top: Ae_62/A-8, bottom: LP447a) after irradiation with 10^{17} p/cm² and 5×10^{17} p/cm², respectively.

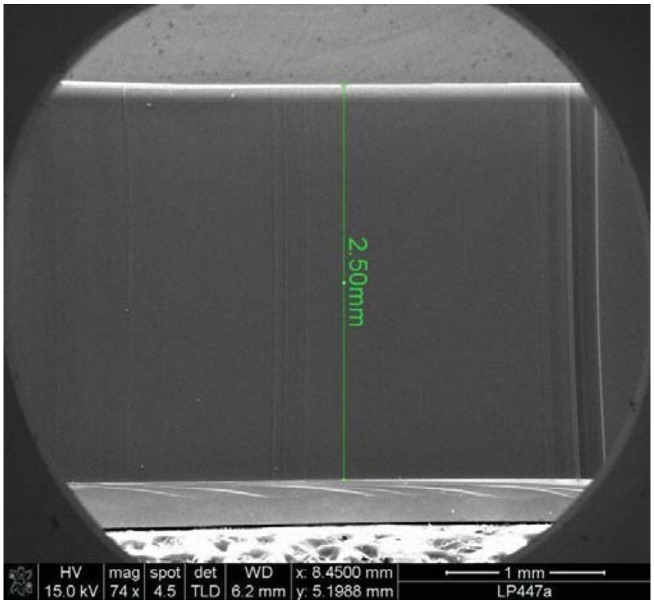

Fig. 5 Electron microscope image of the LP447a sample before irradiation.

the samples with the highest fluence. It seems that the surface changed from a glossy impression to a slightly more matt characteristic.

B. Electron microscope images

A detailed comparison of images taken before and after the irradiation did not reveal any changes in the structure of the samples.

In Fig. 5 an image of the sample that was irradiated with the highest fluence is shown in full size. The extremely regular structure remains unchanged after irradiation. Nowhere along the sample is a detectable change observed.

C. Optical reflectivity

Measurements of the optical reflectivity of the four samples irradiated with increasing dose are presented in table I.

TABLE I. REFLECTIVITY OF VA-CNTS SAMPLES BEFORE AND AFTER PROTON IRRADIATION

Fluence	**Total reflectivity**		
p/cm²	***Sample***	***Before irradiation***	***After irradiation***
1×10^{15}	Ae_54/B-6	3.3%	3.2%
1×10^{16}	Ae_58/A-6	3.1%	3.2%
1×10^{17}	Ae_62/A-8	2.2%	2.5%
5×10^{17}	LP447a	0.8%	1.3%

The same results are also shown in Fig. 6 , this time the change of reflectivity is expressed in dB to compare the data to the respective uncertainty.

The data reveals an increase of reflectivity with increasing fluence, i.e. the absorption decreases. But the residual reflectivity of 1.3% for sample LP447a after a fluence of 5×10^{17} p/cm² is still in the range of conventional absorption layers.

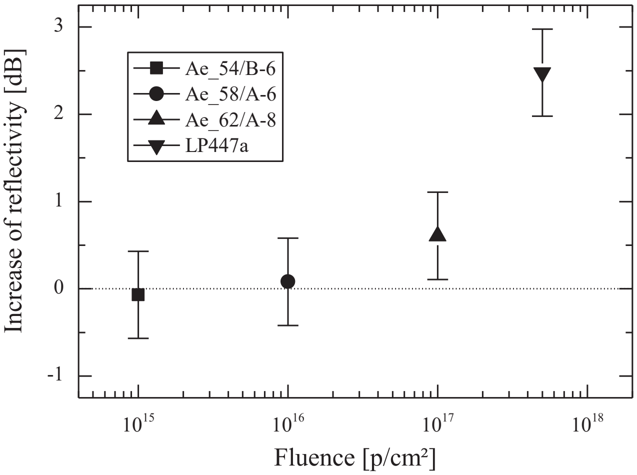

Fig. 6 Increase of reflectivity as a function of fluence.

IV. DISCUSSION

In comparison to our previous work where gamma irradiation up to 11 MGy induced no clearly observable effect on VA-CNTs measured via SEM, optical reflectivity, and Raman spectra [8], protons change the reflectivity noticeable. The results for gamma irradiated VA-CNTs are different to the one obtained with unordered multiwalled carbon nanotubes [12],[13].

The effects of proton irradiation were also investigated before only in unordered VA-CNTs [14]. Here the authors reported on structural changes after irradiation with 70 keV protons up to fluences of 10^{18} p/cm². The nanotubes became amorphous nanowires without internal structure.

Such modifications could not be observed in the present study. Even if the absorption properties changed (see table I) the SEM images showed intact nanotubes. Up to now no HRTEM images could be taken to compare the internal structure of irradiated VA-CNTs to pristine ones.

The high radiation hardness of VA-CNTs compared to unordered samples suggests that the modification of aligned CNTs decreases the possibilities for radiation damage.

V. CONCLUSIONS

To use VA-CNT layers for stray light reduction in satellites the radiation sensitivity has to be investigated. In this paper we show that only at the highest fluences a significant change of the optical reflectivity is observed.

Depending on the orbit and the estimated mission environment the VA-CNTs proved their radiation hardness.

Deviations from former publications that both reported a higher sensitivity to gamma radiation and protons could be due to the difference between aligned CNTs and unordered samples.

Since the currently investigated samples were not specifically optimized for stray light reduction a dedicated project to develop radiation hard VA-CNTs with higher absorption is planned.

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