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Skolkovo Institute of Science and Technology

Thesis Changes Log

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PhD Program: Physics

Title of Thesis: ADVANCED SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBE FILMS BY AEROSOL CVD METHOD FOR ELECTRO-OPTICAL APPLICATIONS

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The thesis document includes the following changes in answer to the external review process.
Prof. K. Kordas: In the Chapter Author's contribution, please indicate your role in writing the manuscripts, and specify what characterization was performed by you. p.VI added author contribution *Prof. S. Shandakov: using abbreviation SWNCT instead SWCNT (for example in Abstract).* p.VII fixed typo: SWCNT *Prof. A. Okotrub: correct and update abbreviation list* *Prof. G. Fedorov:The term "FWHM" should be added to the list of abbreviations.* p.VIII added abbreviation: FWHM - Full width at half maximum *Prof. K. Kordas: The statement "As the equilibrium ratio between metallic and semiconducting nanotubes is~0.5 [19], …" is not true in general, and the cited reference is not appropriate to support the claim. When growing CNTs with similar diameters, the statistical probability for having semiconducting CNTs is 2/3, whereas the rest 1/3 is metallic. This 2 to 1 ratio may be shifted under some unique conditions though.* p.7 text was changed: As the equilibrium fraction of metallic and semiconducting nanotubes is respectively 1/3 and 2/3 [19], tuning the distribution. *Prof. K. Kordas: … the Young's modulus up to 77 GPa is higher than that for the high strength steel) [21]." The cited reference [21] is only a book review and has no such data. The highest reported. Young's modulus of individual CNTs is close to 1 TPa (Nature, 1996, 381, 678–680). Please revise.* Citation was updated: Young's modulus up to 1 TPa is higher than that for the high strength steel) [21]. *Prof. K. Kordas: eq. 2.1, is the Beer-Lambert law, not "Lambert-Berr". On the other hand, if h designates the film thickness, the concentration c shall not appear in the equation. The equation in the current form is valid and used when the absorber is dispersed in a*

nonabsorbing medium. For solids, the usual form of the exponent is a·h, where a is the absorption coefficient and h is the layer thickness. Note, that scattering is ignored

p.10 formula (2.1) was corrected.: the Beer-Lambert law [25]:

$$I = I_0 e^{ah}, \qquad (2.1)$$

where I_0 is the intensity of the incidental beam, *h* is the thickness of the SWCNT film, and *a* corresponds to the wavelength dependent absorption coefficient.

Ph.D T. Susi: Placement of Fig. 2.5 is one line off (breaking a text paragraph)

p.12 figure 2.5 was reshaped

Prof. K. Kordas: In Chapter 2.4, some details on the use of CNTs in solar cells, bolometers and saturable absorbers would be useful. Also here, the sentence "... absorbance within the infrared band allowing to "transform" the photons absorbed into a resistive response [38]" is quite sloppy.

p.15 was clarified role of SWCNT films in different devises:

Recently, solar cells based on amorphous or polycrystalline silicon and SWCNT films used as a transparent window electrode and active p-type layer have shown a superior efficiency in a rigid form and as in flexible devices [37].

Bolometers (photodetectors), where SWCNT films used as a sensing material, are a novel class of devices, which allow to measure the intensity of the infrared wavelength radiation by means of resistance change of the material under its heating [38].

Saturable absorbers are a key component for mode-locking femtosecond lasers. Their working principle is based on non-linear absorption of the light in the material. Single-walled carbon nanotube films have been already developed and demonstrated in the laser applications [40].

Prof. K. Kordas: In Fig. 2.7, to it is not clear how the different applications are related to each other (e.g. how fuel cells are connected transparent electrodes or to transistors)

p.16 figure 2.7 was updated.

Ph.D T. Susi: Using a software screenshot to illustrate UV-Vis-NIR is a questionable choice: it's hard for the reader to understand what it tries to communicate. Also, Fig. 3.2 appears to be based on a preview image of the Kataura plot: if one looks at the original (http://www.photon.t.utokyo.ac.jp/~maruyama/kataura/katauran.pdf), there are no spurious red circles along the x-axis.

p.18 figure 3.2 was updated

Ph.D T. Susi: Raman laser power is not limited only to avoid destroying the sample, but also to avoid heating that causes changes in the response.

p.22 was clarified characteristics of Raman spectroscope:

The laser spot diameter (a 50x objective with numerical aperture of 0.50) on the film surface was about 11.2 μm. In order to avoid the destruction of the SWCNTs during the long exposure and to avoid heating that causes changes in the response, the integral power density of the incident radiation was set at 0.4 $kWcm^{-2}$ when measuring spectra. The obtained spectra were normalized to the intensity of G-peak maxima. Each measurement was taken at least 5 times in different areas of the sample and then averaged; the precision was ±1 cm^{-1}.

Prof. A. Okotrub: Please check the captions and size of all figures (e.g. figure 4.10)

Prof. K. Stevenson: Many of the axes and labels are hard to read as they are too small or even at times cut-off especially in Chapter 4.

Ph.D T. Susi: There is probably a typo in Equation 3.3: I believe the denominator should read "log(10/9)" and the separate (10/9) factor is spurious.

p.24 fixed typo in formula (3.3), added information about during electrical measurements in chapter 4 ware updated figures 4.4, 4.5, 4.6, 4.8, 4.9, 4.10, 4.12, 4.13, as well as figures description.

Prof. G. Fedorov: 7.1 What wavelength range is meant by IR?

p.62 was clarified IR range of bolometer exploitation:

Moreover, the use of various chemical and physical methods for nanotube modification makes it possible to vary their optical and electrical properties over a wide range (in the present research, the studied IR absorption range is 1-30 μm).

p.64 sentence was fixed:

The sensitivity drops significantly with lowering the sample temperature.

Prof. G. Fedorov: Showing R(T) for the films used for bolometers would be helpful as well as comparison of the dark IV curves to those obtained under irradiation.

p.65 figure 7.3 was added, was clarified mechanism on saturable absorbers operation:

If a wave train propogates through a SA, then shortening of the pulse duration is observed because of strong nonlinear absorption (low intensity of the wave train exhibits higher absorption compared to high intensity ones). In this case, SWCNT electronic structure with van Hove singularities could be considered as a classical two-level system favorable for the SA operation».

Ph.D T. Susi: How was the thickness of the coating determined

p.72 was clarified calculation of coating thickness:

(number of layers multiplied by the thickness of a single layer, *i.e.* SWCNT film thickness).

Ph.D T. Susi: How is the spark generator reactor more scalable than the ferrocene reactor, considering the latter has much higher yield

p.75 statement in conclusions was grounded: Precise control over the size of a catalyst particle within a wide range of operating regimes makes the system for the SWCNT synthesis more scalable and stable.

Prof. A. Okotrub: Pleas notice that not all references are in the correct style.

Prof. S. Shandakov: lack of information in some references (9, 13, 14, 28, 41, 63, 64, 67, 74, 76 and 80).

In chapter 9 was fixed like of information in some references

In all text was carried out minor corrections of grammar.