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Thesis Changes Log

Name of Candidate: Daniil A. Ilatovskii

PhD Program: Materials Science and Engineering

Title of Thesis: Rational Design of Single-Walled Carbon Nanotube Films for Transparent Electronics

Supervisor: Professor Albert Nasibulin

Co-advisor: Assistant Professor Dmitry Krasnikov

The thesis document includes the following changes in answer to the external review process.

I sincerely thank the Jury Members for dedicating their time to assess my PhD thesis. I appreciate their overall positive feedback and find great value in the constructive comments and suggestions they provided for enhancing the thesis. In the following sections, I address the specific remarks from each Jury Member.

Response to Prof. Nikolay Gippius

- p.4: please, replace in the abstract the abbreviation TCFs by “transparent conductive films”. This abbreviation is first explained on p. 8 and p.11.

I am thankful to Prof. Nikolay Gippius for the positive review of my thesis. The abbreviation was replaced.

- p.22 (for -> from) high- to low-temperature zone

The correct preposition was replaced.

Response to Prof. Dmitry Gorin

1. PhD thesis contains three main aims, could you explain an interconnection between them?

I want to express my gratitude to Prof. Dmitry Gorin for providing constructive feedback on my thesis. The interconnection between the three aims of the work (deposition, doping, and rational design) lies in the big goal of enhancing the optoelectronic performance of SWCNT films for applications in next-generation electronics. It is based on the approach towards optimizing various stages of SWCNT film fabrication, from deposition to post-deposition modifications. The deposition step addresses the challenge of selectively depositing SWCNTs based on their chirality or metallicity, contributing to the overall control of film properties. The doping step targets finding alternative doping materials that not only enhance conductivity but also provide long-term stability in the optoelectronic properties of the doped SWCNTs. Rational design is applied both during the deposition stage (influencing film morphology) and in the post-deposition stages (influencing the overall structure and properties of the final SWCNT film). In our work, we pointed out the final destination of the rational design for the best optoelectronic performance of SWCNTs to help other scientific groups in the development of this approach. The last paragraph of the Introduction was changed to pay more attention to the interconnection of all three approaches.

2. Page 24, Figure 4, How we can obtain the positive and negative photophoresis in the frame of this work? Is it possible to realize it using only the wavelength variation?

According to the theory by Rubinowitz [1] and the discussed model (eq. 4.9 and 4.13), we consider SWCNT as a highly absorbing particle possessing only positive photophoretic motion (direction coincides with the vector of light propagation), which was proved by experiments. This information was added after Fig. 2.4. The mechanism is explained *via* photophoretic asymmetry factor J_1: it has a negative value (from 0 to -0.5) for carbon nanotubes, which makes photophoresis positive (velocity has positive sign; eq. 4.9 and 4.13). J_1 will be discussed in detail in question 4.

3. I would like to know your opinion on the combined use of thermophoresis and photophoresis simultaneously for selective deposition? Do you expect a synergy effect in this case?

I express my gratitude to Prof. Dmitry Gorin for this interesting idea of the synergetic effect of two processes. According to the known data [2,3] and the experiments done in the Laboratory of Nanomaterials, the temperature gradient for the thermophoretic process is exceptionally high, which results in efficiency higher than 90%. Thermophoresis would exceed the effect of photophoresis, which has a weaker nature, as well as would lose the selectivity effect. On the contrary, according to the recent results obtained by our team, the thermophoretic effect is chirality independent providing the deposition of every nanotube within the ensemble. Thus, it is unreasonable to make the combination of two processes as thermophoresis is required for the effective deposition of all the nanotube species, while photophoresis shows a potential to be useful for the deposition of specific fractures of SWCNT ensemble.

4. Page 44, Figure 4.3, Do you have explanation of the changes of the fine structure of RBM peaks on Raman spectra with and without LED- irradiation? Could you explain the mechanism behind of the chiral selectivity of deposition through light irradiation (page 45, Figure 4.4.)?

The mechanism of selectivity leading to a redistribution of RBM peak intensity is highly important and is to be explained. Following the theoretical discourse, parameter J_1, representing the photophoretic asymmetry factor (as described in equations 4.5 and 4.6), includes both the real and imaginary components of the complex refractive index of SWCNTs at the irradiation wavelength [4]. We have introduced equation (4.20) to define J_1 for a spherical particle [5]:

$$J_1 = 4\pi n\kappa\frac{\alpha}{\lambda}\left(\frac{3(n-1)}{8n^2} - \frac{4}{5}\pi n\kappa\alpha\right),$$

where n and κ denote the real and imaginary parts of the complex refractive index, respectively, and λ represents the wavelength of irradiation. Since the refractive index varies for different chiralities, in cases of positive photophoresis, J_1 can range from -0.5 to 0 [6]. The photophoretic motion does not occur at J_1 = 0, while it reaches its maximum at -0.5. This aligns with equations 4.9 and 4.13, facilitating the selective deposition of SWCNTs.

Overall, according to the chirality, SWCNTs have different photophoretic velocities at a wavelength of irradiation, which results in different efficiency of deposition. SWCNTs with chiralities possessing high efficiency, demonstrate increased intensity of corresponding RBM peaks for deposited samples. The information was added before Table 1.

5. Page 63, Figure 4.16 c, what do you expect the subsequent increase in the number of layers in the films for example.

The idea of increasing the number of layers is essential to be discussed. In the model, we consider ideal "armchair" nanotubes, which have the same values of quantum resistance for all chiralities and lengths. If we increase the number of layers, the resistance will be higher because of the contact between layers and the scattering of charge carriers [7]. We can observe this effect even for a 2-layered film: it has a resistance of 6.84 kΩ, compared to 6.46 kΩ for a 1-layered one. During higher stacking, we will both increase resistance and decrease transmittance of transparent conducting films, both effects decrease R_{90} value. Thus, the subsequent increase in the number of layers results in a decrease in the performance of SWCNT film.

Response to Asst. Prof. Stanislav Evlashin

1. How many experiments were carried out in electrophoretic deposition and AFM studies?

I would like to thank Asst. Prof. Stanislav Evlashin for the high assessment of the thesis. Indeed, the data of a number of the experiments is to be added. Samples were collected at least 3 times at each

time (15, 30, 45, and 60 minutes); while AFM scans were done 10 times in different spots for each sample. The information was added in the experimental part.

2. If temperature flow is the determining factor, then it would be a good idea to make estimates of the absorption of metal and semiconductor tubes. Since the absorption of such tubes will be different, this will also affect the deposition.

I agree with this comment that the interaction between SWCNTs with different metallicity/chirality and light irradiation should be described in detail. According to the added equation 4.20, factor J_1, (included in eq. 4.5 and 4.6) depends on the real and imaginary parts of the refractive index at a certain wavelength of irradiation, which differs for different chiralities. It may vary from $J_1 = 0$ (zero motion) to -0.5 (maximum motion) [6], according to eq. 4.9 and 4.13. Thus, SWCNTs with different chiralities have different photophoretic velocities according to their refractive index at a certain irradiation wavelength. Equation 4.20 is:

$$J_1 = 4\pi n\kappa\frac{\alpha}{\lambda}\left(\frac{3(n-1)}{8n^2} - \frac{4}{5}\pi n\kappa\alpha\right),$$

where n and κ are real and imaginary parts of complex refractive index, λ – wavelength of irradiation. Our study is a pioneer work, that started the development of the strategy to deposit SWCNTs from an aerosol state, and, hopefully, it will set a for further theoretical and experimental projects on the topic, which would include calculations on a higher level. The information was added before Table 1.

3. How many samples were analyzed in Table 1?

The question is highly reasonable for understanding experimental reproducibility. We analyzed 3 samples; each of them was measured at least at 5 different positions. We have added it in the Experimental section.

4. It is not clear why the positions of the points on graph 4.5 move so much.

We should discuss photoluminescence data in detail. First, the existence of PL peaks beyond the irradiation zone could suggest the deposition of SWCNTs resulting from Brownian diffusion. Second, the initial SWCNTs used for laser deposition displayed broad diameter distributions with optical absorption peaks partially overlapping the 1550 nm laser wavelength. To enhance data representativeness, we employed not only the excitation at the E22s transition (910 nm) of tubes emitting at approximately 1550 nm but also wavelengths (467 nm and 595 nm) resonant to tubes with diverse diameters. Emission distributions (Fig. 4.7) for all excitation wavelengths exhibit saturation in the 1500-1600 nm range, aligning with the irradiation laser spectrum. This is likely attributed to the deposition of SWCNTs with absorbance peaks from Table 2. We added the normal probability plots of PL distribution (Fig. 4.7) and Table 2 to make the data more representative.

5. When using a 6 W LED, what is the radiation intensity per nanotube stream, taking into account the chamber design?

We thank Asst. Prof. Stanislav Evlashin for paying attention to the light irradiation intensity. 6 W is the resulting power of the light beam for the transparent window (5×5 mm^2) of the photophoretic cell, which can be considered as radiation intensity per SWCNT flow. We have pointed out in the experimental part, that this value is the resulting, not the initial one.

Response to Prof. Maoshuai He

1. The excitation laser wavelengths of acquired Raman spectra should be presented in the captions of Figure 4.3, 4.4, etc.

I am grateful for the thorough and valuable review by Prof. Maoshuai He. The Raman measurements (Figures 4.3 and 4.4) were carried out using a 633 nm excitation laser. The corresponding data were added to the captions.

2. In Figure 4.6, the UV-vis-NIR absorption spectrum of collected SWCNTs without light irradiation could be presented for comparison.

I agree with Prof. Maoshuai He that the graph should be explained in detail. As we changed the condition of SWCNT synthesis, we checked the properties according to UV-vis-NIR spectra. Fig. 4.6 shows the absorbance spectra of pristine SWCNTs without light irradiation together with the spectra of light emission to demonstrate their intersection. The corresponding information was added before Fig. 4.6.

SWCNTs deposited on a quartz substrate form ultrathin films or rarified bundles, so the difference between samples with- and without light irradiation cannot be compared by absorbance spectroscopy. We produced measurements of UV-vis-NIR spectra for samples deposited on the filter after the photophoretic cell (Fig. 3.1) with- and without excitation as well. However, due to the rather low efficiency of deposition and only partial selectivity, the difference between samples does not overcome the fluctuations, which makes the method irrelevant for any comparison. Alternatively, we carried out Raman measurements with deconvolution of chiralities (LED) and photoluminescence data (PL) to prove the partial selectivity of photophoretic deposition.

3. The reasons for the different (n,m) intensities shown in Table 1, could be discussed in more details.

Prof. Maoshuai He is correct that the question of chiral selectivity is to be expanded. According to the adapted theoretical discussion, the photophoretic asymmetry factor (equations no. 4.5 and 4.6) includes real and imaginary parts of the complex refractive index of SWCNTs at a wavelength of irradiation [4]. We have added eq. (4.20) for the definition of J_1 for a spherical particle [5]:

$$J_1 = 4\pi n\kappa\frac{\alpha}{\lambda}\left(\frac{3(n-1)}{8n^2} - \frac{4}{5}\pi n\kappa\alpha\right),$$

where n and κ are real and imaginary parts of complex refractive index, λ – wavelength of irradiation. As the refractive index differs for various chiralities, in the case of positive photophoresis, J_1 may vary from -0.5 to 0 [6]. At $J_1 = 0$, photophoretic motion does not appear, while at -0.5, it has the highest value, in correspondence with eq. 4.9 and 4.13, which provide selective deposition of SWCNTs. The paragraph with this explanation was added after Fig. 4.4.

4. In the last section, it is revealed that parallel SWCNT films consisting of (4,4) SWCNTs exhibited a low R_{90} values. Have the authors considered the stability of the SWCNTs? Owing to the large curvature, SWCNTs with so small diameters are likely unstable under ambient conditions.

The question is reasonable because the thesis is oriented toward further production of applied materials. We agree that SWCNTs with high curvature mostly present as the inner layer of double-walled carbon nanotubes, so if we consider SWCNTs with lower curvature, e.g. (10,10), R_{90} would have the same order of magnitude (Fig. 4.17). Thus, this important question leads to the conclusion that section 4.3 conceptualizes the ideal isolated case of SWCNT film to define the final destination for the entire topic; and the main discovery of the modeling is the μΩ-magnitude of theoretical sheet resistance, which can be called a fundamental limit. We are grateful for this notice, and the corresponding remark was added after Fig. 4.17.

Response to Prof. Ying Tian

I highly appreciate the comprehensive review by Prof. Ying Tian.

References:

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