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Thesis Changes Log

Name of Candidate: Javier Antonio Ramirez Benavides

PhD Program: Materials Science and Engineering

Title of Thesis: Advanced single-walled carbon nanotube membranes for opto-electro-mechanical applications.

Supervisor: Prof. Albert Nasibulin

Co-supervisor: Assistant Professor Dmitry Krasnikov

The thesis document includes the following changes in answer to the external review process.
Dear Jury, I appreciate the effort and time of the reviewers for their analysis and comprehensive recommendations about the presented work. In the following text I will provide a comprehensive response where required as well as manuscript updates where the request is reasonable and deemed it as necessary. Otherwise, an explanation will be provided justifying why the changes were not made, or not applicable. Thank you for helping me to improve the manuscript! To help the navigation, the code is the following: • Q: Stands for questions • R: stands for response / answer • C: stands for correction / change request • **Green text denotes details where additions, changes and or citations were made to the final manuscript.**

Response to Professor Dmitry Gorin

Thank you for revising these important composition mistakes.

1) C: Page 34, Figure 7 (SEM images), Page 35 (SEM image), Figure 8. Please add info about size of the scale bars to the figure captures.

R: Info about scale bars was added to Figures 7 and 8.

2) Q: Page 71, Figure 27. Why do you have 3 curves (black, blue, and red) in the insert? Black means pristine. Red means ethylene. What does mean a blue curve?

R: Blue curve was eliminated from the inset of Figure 27.

3) Q Page 71, Figure 27, page 85 Figure 37. I recommend to evaluate the carbon nanotube diameter based on analysis of RBM peaks.

R: Raman spectroscopy is one of the most important powerful techniques to study carbon nanomaterials, however can examine only a small fraction of SWCNTs, which are in resonance with the energy of the laser used for the measurements. An useful reference towards understanding RBM diameter assessment is in: Analysis of the Size Distribution of Single-Walled Carbon Nanotubes Using Optical Absorption Spectroscopy Ying Tian *et al.* The Journal of Physical Chemistry Letters 2010 1 (7), 1143-1148 DOI: 10.1021/jz100161p. According to the authors, the assessment of radial breathing modes can be approximated using the following simplified formula:

$$\omega_{RBM} = \frac{A}{d_t} + B$$

Where the values obtained experimentally were: A=217.8 and B=15.7 (for ω_{RBM} in cm^{-1} and d_t in nm)

Y. Tian, H. Jiang, J. v. Pfaler, Z. Zhu, A. G. Nasibulin, T. Nikitin, B. Aitchison, L. Khriachtchev, D. P. Brown and E. I. Kauppinen, J. Phys. Chem. Lett., 2010, 1, 1143–1148.

Therefore, the RBM is not fully representative to conclude about the diameter distribution of SWCNTs and rather qualitative. To estimate the diameter of the nanotubes we used TEM images. The measured diameters are given in the text, RBM was included only to confirm the presence of SWCNTs.

4) C: Page 100, The unit of pressure is Pa instead of pa, please use kPa instead of Kpa.

R: Units were corrected as suggested in page 100.

Response to Professor Oleg Tolochko

Thank you for the time you invested in formulating interesting questions.

1) C: Some carelessness in the design of the work, for example, Fig.1 (f, g, h) exists, however there are no (f, g, h) in the figure caption; there no authors surnames in the Ref.1, etc.

R: Caption was fixed and f, g, h was added for Figure 1. Ref 1 is fixed and now contains surnames. All other references were verified and corrected as necessary.

2) Q: Too much attention was paid by the author to carbon modifications and nanotube synthesis methods, more than 30 pages in the thesis. However, this information has been already well known to researchers, who deals with nanocarbons. At the same time, only 5 pages show CNT membrane applications and aerosol protective pellicles. It is not enough for full understanding of problems of this research work.

R: The aim of the presented literature review is far from sparking debate about trends in CNT synthesis, but to provide the reader with a comprehensive review about membranes; their production method is critical because their features are heavily dependent on parameters like the length of the nanotubes obtained, the amount of structural defect, presence and amount of contaminant, catalyst residues among others. It is noticeable that the amount of existing literature using CVD to produce SWCNT membranes is limited. Hopefully the presented work could be considered as a contribution towards enlarging the current *scientia ac labore,* related to high quality, synthesis of SWCNT combined with fil and membrane production.

The functionalization of carbon nanotubes was extensively investigated due to their critical role in providing the most advantageous methods for material engineering. This research specifically required high-quality, low-defect single-walled carbon nanotubes (SWCNTs), and realize electric resistivity and optical membrane engineering. Without this thorough exploration, the selection of efficient and ecologic functionalization of membranes for the proposed applications would remain uncertain.

Each section of the literature review corresponds to a matching counterpart in the results sections, thereby addressing the key elements of the selection criteria for the synthesis method. This approach ensures the production of materials capable of functioning under the considered environment. Condensing this section could potentially compromise the quality of relevant background information regarding the optimal synthesis process and the drawbacks of alternative methods.

The manuscript focuses primarily on two niche technological applications. Consequently, expanding the section devoted to applications was deemed beyond the scope of this research, as it pertains to future investigations. There is a substantial amount of published literature available on this topic, and our proof of concept within the results section expands the potential applications for the welded membranes.
The current five-page structure appears sufficient to elucidate the research goals, that are explained further in the results and conclusions. For a comprehensive understanding of this work, particularly the results and prospective applications, it is crucial to note that this research, presents a focused selection of industrially relevant applications.

To fully grasp the implications of this research, especially the results and potential applications, it is essential to consider that the work presented is not an exhaustive literature review on CNT membrane applications. Rather, it offers a targeted examination of industrially relevant applications. Due to the above motivation, respectfully considering your kind comment, the decision of keeping the text of the literature review unaltered was taken, to maintain the integrity and focus above explained.

3) Q: Why the author don not try 20 min welding? It would make an increase in the filtering efficiency and mechanical properties of membranes.

R: Welding times of up to 1 hour were tested, 20 minutes are included within the results. A look to Figure 42 in the manuscript allows us to infer that:

The longer the welding time, the more carbon is deposited on the surface of SWCNTs. More carbon growth around the SWCNTs means less area for “pores” (less area for gas to pass through in the case of a filter), but this benefits mechanical applications because it reinforces the film, so beyond 40 minutes we end up with a film composed of carbon, with nanotubes buried within the structure, with few or no pores, with an optical transmittance of less than

10%. Thus, after 40 minutes of welding we obtained a membrane that functions as a very low efficiency filter and more useful as a conductive optical attenuating carbon film, or a super strong carbon film, rather than a transparent electrode, because the film becomes somehow reflective and shiny. Since the scope of application of this manuscript is high efficiency filters for special aerosols, and highly conductive transparent electrodes, we chose the acceptable transmittance loss of 1% maximum for transparent electrodes and 50% maximum for films towards mechanical applications. Thus, these results of welding more than 40 minutes have characteristics that do not fulfill the criteria for the presented applications, but are useful for future research and develop new applications where the strength and chemical inertness are paramount.

4) Q: Why does the equivalent sheet resistance R90 (Ω/□) of welded and doped CNT grow up that insignificantly?

R: The primary objective of the welding process was to enhance gold chloride doping, thereby minimizing sheet resistance to the greatest extent possible. The negligible increase in R90 was intentional, designed to maintain a material with both high transparency and high conductivity. It's important to note that extending the treatment duration does not lead to improved doping. Instead, prolonged treatment results in increased absorbance, which, while potentially enhancing mechanical robustness, compromises optical transmittance. This trade-off ultimately diminishes the material's effectiveness as a transparent electrode. The challenge lies in optimizing the welding process to achieve the ideal balance between conductivity, transparency, and mechanical stability, ensuring the material's suitability for its intended application as a high-performance transparent conductive film.

5) Q: Is that in the frames of experimental error?

R: The correct application of error propagation is crucial for the accurate interpretation of optical and electrical measurements, used in this case for the conclusions around R_{90} before and after the treatments presented in this work. This work cares for precise characterization of properties, it is essential. Neglecting proper error propagation can lead to misinterpretation of data, overestimation of measurement accuracy, and potentially flawed conclusions about material behavior. Considerations were given for the presented data, in the table 1, page 96: the error propagation with correlation treatment was applied, 10

exemplars of each treatment were elaborated, their measurements averaged, and our combined experimental error calculated as follows in an over simplified manner:

Assuming a correlation coefficient of ρ = -0.7 (Negative correlation), using the method explained in the next issue (#6) the obtained uncertainty of R_{90} for the sample of interest was: 30 ± 0.92, so the obtained measurements are out of the frame of experimental error, considering also the manufacturer data of error and uncertainty of the used instruments: Jandel RM3000 four probe station, and Perkin Elmer Lambda1050. There is no consensus about the most advantageous method for assessing the combined error, as briefly explained in the next issue.

6) Q: Was there any statistical analysis of the results

R: Yes. We used error propagation with correlation (as explained on the previous issue): This method accounts for the correlation (ρ) between R_s and T_{av}, which is crucial for TCMs. The figure of merit (FOM) R90 for transparent conductive materials (TCMs) doesn't have a single, universally agreed-upon "complex error" calculation. The complexity arises because R90 itself is a composite metric derived from two often-correlated measurements: sheet resistance (R_s) and average transmittance (T_{av}). The error calculation needs to account for the correlation between these primary measurements.

When calculating the uncertainty in a function of multiple variables, we need to consider the uncertainties in each variable and their correlations. In this case, both R_s and T have uncertainties, and they might be correlated (e.g., a measurement error in one could influence the other).

The general formula for the propagation of uncertainty with correlated variables is:

$$\mathrm{Var}(\mathrm{R90}) \approx \left(\frac{\partial \mathrm{R}_{90}}{\partial \mathrm{T}_{\mathrm{av}}}\right)^2 \mathrm{Var}(\mathrm{T}_{\mathrm{av}}) + \left(\frac{\partial \mathrm{R}_{90}}{\partial R_s}\right)^2 \mathrm{Var}(R_s) + 2\rho \left(\frac{\partial R_{90}}{\partial T_{av}}\right)\left(\frac{\partial R_{90}}{\partial T_{rs}}\right)\sqrt{Var(T_{av})Var(R_s)}$$

Where:
$\mathrm{Var}(T_{av})$ and $\mathrm{Var}(R_s)$ are the variances of T_{av} and R_s;
ρ is the correlation coefficient between T_{av} and R_s.

Var(T_{av}), Var(R_s) and ρ need to be determined experimentally (e.g., from repeated measurements).

Calculation of Variances: $VarR_s = \sigma {R_s}^2$ and $VarT_{av} = \sigma {T_{av}}^2$

Considering: $R_{90} = \frac{{T_{av}}^{10}}{R_s}$ the partial derivatives are: $\frac{\partial R_{90}}{\partial T_{av}}$ and $\frac{\partial R_{90}}{\partial R_s}$

Calculation of the standard deviation: $\sigma R_{90} = \sqrt{Var(R_{90})}$

With the above explained method we ensure the understanding of the accuracy related to the error of the presented measurements and calculations, and the certainty of the presented conclusions.

7) Q: How many samples were studied?

R: More than 100 samples were studied to optimize welding procedure and to decrease R_{90} as much as possible for the application as transparent conductive electrode and maximize ultimate tensile strength for the application as filtering membrane.

Response to Professor Stanislav Evlashin

Thank you for the time you invested in formulating interesting questions, that enhance the current contents and future research of the presented work.

1) Q: I would like to know about the stability of the structures under EUV radiation over an extended period.

R: Thank you very much for this very important question! Unfortunately, the long-term stability tests for our samples were not possible, since we do not have the appropriate facilities. However, there are a few commercial products based on aerosol CVD SWCNT for EUV applications https://canatu.com/company/carbon-age-news/cnt-is-the-material-choice-for-the-most-advanced-euv-pellicles/. Due to the hexagonal carbon single atom thick mesh structures of CNT, their absorption of EUV radiation is very low compared to continuous films, combined with the low power of the light sources used for semiconductor production in the order of hundreds of watts and the fact that the scanner environment have a very low amount of oxygen, seem to not to damage the CNT films at all.

The CNT-based pellicles are popular in the industry. Nonetheless, they still need to be replaced when the optical transmittance becomes unacceptable for the lithography process, when too much InSn / Sn aerosol coats them and stops the EUV light from passing through. The films are normally replaced without breakage, despite the extra metal mass which tells that the mechanical sturdiness is kept to a great extent. Since previous renewal technology did not exist, possibly the study was impossible due to the material deposition unless a second pellicle exists in the system to protect the CNT film from the light source produced aerosol. The effect of EUV photon energy on CNT seems not important (if any), and the thermal effects are negligible, since the thermal stability of our membranes in presence of oxygen (air) is proved to *ca.* 350°C and in vacuum ($3x10^{-7}$ Torr) is of around 1500°C, the power of an EUV light source has to be very high for causing measurable damages to the CNT structures (kilowatts/cm^2). A formal, specific study of CNT stability under long term EUV could not be found at this moment, but some related literature is:

Radovan K. *et al. "*Thermally stable near UV-light transparent and conducting SWCNT/glass flexible films", Carbon, Volume 152, 2019, Pages 7-15, ISSN 0008-6223, https://doi.org/10.1016/j.carbon.2019.04.053 .

Timmermans M. *et al.* CNT EUV pellicle tunability and performance in a scanner-like environment, 11609, SPIE Advanced Lithography, 2021, https://doi.org/10.1117/12.2584519

Sumit K. *et al.* An investigation on thermal stability of single wall carbon nanotubes (SWCNTs) by molecular dynamics simulations, Materials Today: Proceedings, Volume 44, Part 6, 2021, Pages 4940-4944, ISSN 2214-7853, https://doi.org/10.1016/j.matpr.2020.11.1026.

Timmermans M. *et al.* "CNT EUV pellicle tunability and performance in a scanner-like environment," Proc. SPIE 11609, Extreme Ultraviolet (EUV) Lithography XII, 116090Y (23 March 2021); https://doi.org/10.1117/12.2584519.

According to the last reference, exposition during 15 min @ 600W EUV causes transmissivity changes in the CNT films studied. Our power figures were of 100-150 W EUV, and commercial applications reach 150 W, less than half the threshold for damage according to abovementioned reports. Last but not least, according to our discussions with EUV source development team from IS RAS, it is plasma not EUV itself that harms the most.

2) Q: What is the service life of different membranes under this type of radiation?

R: The service life of the membranes is inversely proportional to the power of the EUV light source. This happens because at higher power, more “shots” of SnIn / Sn plasma are produced, thus more aerosol. If the pellicle operates continuously hot, or in “continuous renewal” at commercial power of 100 to 150 Watts of EUV light, the previous paper has some details about this particular. The shadowing by deposited aerosol of SnIn / Sn is much faster than the degradation of nanotubes, especially at low power; if the scanner is operated continuously, and the film is constantly hot, the degradation of the pellicle predominates because no aerosol will stick to the CNT film. For this scenario the expected service life of 60% SWCNT renewable pellicle would be of weeks, until the membrane breaks.

Timmermans M. *et al.* "CNT EUV pellicle tunability and performance in a scanner-like environment," Proc. SPIE 11609, Extreme Ultraviolet (EUV) Lithography XII, 116090Y (23 March 2021); https://doi.org/10.1117/12.2584519.

3) Q: Why do Sn and In not penetrate through the membrane during annealing?

R: Thank you for such an interesting question. During annealing, the randomly stacked SWCNT membrane used in question has nanotubes of ~ 2nm diameter. Droplets of In and Sn are bigger than this, and in any case, particles of sizes < 10nm tend to form bundles and are susceptible of being trapped by the mechanisms responsible of trapping matter in filters. Indeed, HEPA or Petryanov filters – the common standard nowadays has fibrous morphology with micrometer-thick individual units. SWCNT have the same morphology but the size almost 3 orders of magnitude lower allowing even higher efficiency This is how the membrane works as a filter for aerosol. In and Sn can exist only in vapor phase at annealing conditions ($3x10^{-7}$ mbar, 1300°C), and this vapor tends to condensate in the colder parts of the vacuum chamber surrounding the membrane. One could assume that the vapor, given the gas permeability of the membranes does penetrate. In the article "InSn plasma penetration through protective single-walled carbon nanotube-based membranes" by V. Gubarev *et al. From Applied Physics Letters 121,141901 (2022)* *https://pubs.aip.org/aip/apl/article-abstract/121/14/141901/2834365/InSn-plasma-penetration-through-protective-single?redirectedFrom=fulltext*, this question is partially answered:

> "Faraday cup measurements show that 40- and 90-nm-thick SWCNT membranes reduce the total charge transition by 20 and 130 times, respectively. The ion analyzer measurements demonstrate that ions pass through the membrane mainly due to the collision less (ballistic) mechanism. Using scanning electron microscopy, we estimate a decrease in a plasma (ions + atoms) flux to be of 18 and 140 times for 40- and 90-nm-thick SWCNT-based membranes, respectively."

There is an attenuated flow of ions, and plasma flux attenuation is also estimated. Residual surface InSn was not detected post renewal by EDX mapping, and optical EUV-UV-Vis-NIR transmittance was restored for every case.

4) Q: How do films degrade with fluence at EUV?

R: I assume your question deals with radiant exposure. The effect seems to depend on the concrete type of nanotubes composing the material exposed. For our case (SWCNT), no changes were observed. Mechanical tests were not performed post renewal. The reason is that the material works correctly for the presented application as long as it will not be broken.

In other words, if the membrane is in one piece, with no visible tearing or orifices, it will still function. According to post exposition SEM and Raman measurements, the samples did not exhibit degradation. There is a report entitled: “Damaged carbon nanotubes get healed by ion irradiation” https://doi.org/10.1063/1.3466774 by K. Jeet *et al.* from the Journal of Applied Physics 108, 034302 (2010) that is able to explain why no degradation was observed. Nevertheless, also exists: Effects of ion irradiation on carbon nanotubes: a review https://doi.org/10.1504/IJMPT.2012.051328 by Y. Zhang *et al.* from the International Journal of Materials and Product Technology 45, 1-4, (2013) where some of the reports evaluated by the authors conclude about the nanotube defect creation after exposure. Again, the conditions of radiation exposition, same as for us can heal or damage the structures. Since our data reflects no degradation, and our conditions of operation are dissimilar to the reports indicating damages, the issue was regarded as unimportant for our presented research. Text was not changed due to this regard.

5) Q: Given that EUV radiation is quite energetic, it should lead to rapid degradation not only of nanotubes but also of other carbon materials. I would also like to see data on changes in mechanical characteristics due to fluence. Please provide relevant literature.

R: The power damage threshold observed by Timmermans *et al.* for CNT membranes and EUV exposition starts at around 600 W during 15 min. Such intensity for EUV is not common for industrial IC EUV lithography scanners. For our tests lasting around 30 minutes, using around 150 watts of power. The degradation of the membrane was not confirmed. Observation in SEM, TEM and Raman Spectroscopy confirmed that the heat treatment heals defects on the carbon nanotubes, effectively improving their quality, decreasing the intensity of D peaks for annealed and renewed membranes. A CNT membrane in ambient conditions, exposed to humidity and oxygen will have accelerated degradation compared to a low pressure, pure helium rich, ppb water levels inside of a EUV lithograph. Data about changes in mechanical characteristics due to fluence, are future research, out of the scope of the presented application for the studied samples, nevertheless, the following reports can be useful:

“Damaged carbon nanotubes get healed by ion irradiation” by K. Jeet *et al.* from the Journal of Applied Physics 108, 034302 (2010) https://doi.org/10.1063/1.3466774

"Effects of ion irradiation on carbon nanotubes: a review" by Y. Zhang et al. from the International Journal of Materials and Product Technology 45, 1-4, (2013) https://doi.org/10.1504/IJMPT.2012.051328.

Your previous question is related to this one, in order to avoid redundancy, here a more technical explanation is provided. No changes to the manuscript were made with respect to this regard.

6) Q: The work studies the properties of structures under EUV conditions; however, the characterization of optical properties is provided only for the visible range. Have studies been conducted with EUV on welded tubes? How did the use of HAuCl4 affect absorption in wavelengths shorter than 100 nm?

R: The work presented uses UV-Vis-NIR characterization as one element of collective standard methods to assess the presence, diameter and quality of single-walled nanotubes in the films used for the investigation. No studies were performed with EUV on welded nanotube membranes because the elimination of the slip tube-tube mechanism leads to non-elastic films. The annealing process itself causes some degree of welding, but the mechanical quality changes are negligible. The extra mass of the deposited carbon also harms transmissivity on EUV, which is undesirable. The *in-situ* investigation had no broken membranes, so the mechanical sturdiness of pristine membranes proved sufficient for 10 renewal cycles at least.

Since the scope of application for $HAuCl_4$ doped films is completely different and away from EUV and the higher electric conductivity produced by it does not bring any advantages to the EUV SWCNT based renewable pellicle, it was not even considered. Because of this the $HAuCl_4$ doped SWCNT film absorption for optical wavelengths under 100 nm was not studied during the course of this work.

7) Q: Is it appropriate to conduct mechanical tests on bundles and compare them with films after the modification?

R: The membranes used for this research are composed of randomly oriented stacked (bundled) carbon nanotubes, as it has been reported by other groups and confirmed by the micrographs presented in the thesis, during the process of synthesis and collection of

carbon nanotubes bundles of them are formed. Since we have an abundant amount of carbon nanotube bundles composing the bulk of the membranes, it is not practical to isolate the bundles for any of the technological problems presented on this work. The closest comparison of “bundles” for the size scale of the presented films would be SWCNT based fibers, this is an active area of research, but unfortunately the fibers tend to have poor transparency and are not suitable to be used ad optical elements.

8) Q: Is there a rearrangement of nanotubes during welding, or does an amorphous layer grow without rearranging nanotubes in the contact zone? It would be beneficial to perform XPS analysis to determine sp3 and sp2 carbon content depending on the welding mode. What does the literature indicate regarding this.

R: The microscopy observation shows that the randomly oriented stacked arrangement of SWCNT is kept during all processes presented on this research, moreover the assessment of filtration quality for the welded SWCNT membranes is more or less the same, so the average pore size and distribution is almost not modified. From these facts, we can infer that no rearrangement of nanotubes happened during the course of the presented processes to which SWCNT membranes were exposed.

For long periods of welding, no nanotube rearrangement happens. The network is coated by carbon, maintaining the original nanotubes in the original positions inside. The specific nature of this carbon allotrope produced by pyrolysis of Ethylene gas is unknown from the analysis performed. The presence of crystalline structures was discarded in the carbon surrounding the SWCNTs by the electron diffraction observation. Most probably the structure is amorphous-vitreous. The investigation of XPS is indeed useful to elucidate the hybridization. Nevertheless, the fraction of “welded” carbon (as it presumably appears at SWCNT junctions) will be relatively low which is proven by UV-vis-NIR absorbance spectra. Thus, we believe it would be extremely hard to unambiguously distinguish the exact signal from “welded” carbon.

Previous reports like:

Song Jiang *et al.* Ultrahigh-performance transparent conductive films of carbon-welded isolated single-wall carbon nanotubes. Sci. Adv. 4, eaap9264 (2018). https://doi.org/10.1126/sciadv.aap9264.

A.N. Obraztsov, *et al.* Chemical vapor deposition of thin graphite films of nanometer thickness, Carbon, Volume 45, Issue 10, 2007, Pages 2017-2021, ISSN 0008-6223, https://doi.org/10.1016/j.carbon.2007.05.028.

The abovementioned references do not mention the types of hybridization present on their products. Since we are dealing with carbon-carbon composed structures, and 2D materials, it is possible to discard SP hybridization. Graphite and graphene are solely SP^2 in a hexagonal lattice (graphene like). Only different than hexagonal carbon allotropes, like diamond possess SP^3 orbital hybridization.

Qilong Y. *et al.* "All-carbon devices based on sp2-on-sp3 configuration." APL Mater. 1 March 2019; 7 (3): 030901. https://doi.org/10.1063/1.5082767

Also, our colleagues, directed by Dr. Julia A. Baimova from the "Institute for metals super plasticity problems of the Russian academy of sciences", contributed with simulations about welding of carbon nanotube, and the conclusion was that around the Schottky barriers, the CVD synthesis of stacked graphene happened for the presented welding process. Thus, sp^2 was present.

Response to Dr. Yulia Ioni,

Thank you for the time you invested in reviewing and formulating a meaningful amount of form corrections that improved quality and readability of the presented work.

1) The text contains a large number of syntax errors (extra spaces, paragraph breaks, and missing punctuation marks), and in some places it is difficult to read. The figure captions are not consistent, namely, after “Figure No” there is either a colon, a period, or there are no any punctuation marks. The term “Joule heating” sometimes written with a lowercase letter.

R: Non-printable extra characters were eliminated and alignment corrected. Consistency in Figure captions is revised and corrected where necessary as indicated also in previous issues. Punctuation marks were revised, Text was analyzed and improved using artificial intelligence in an attempt to improve readability. Joule heating was changed to upper case in all instances.

2) The list of abbreviations should be supplemented with abbreviations present in the text: PTFE, MCD, HEPA. Abbreviations should be used consistently. The text sometimes contains chemical vapor deposition, sometimes CVD; sometimes ultraviolet, sometimes UV, etc. Also, multiple abbreviations should be removed from the text (for example, on page 60 – DC).

R: The suggested abbreviations were added to the corresponding parts. Consistent use was revised, and as of APA recommendation, explained only on the first mention. Multiple mentions were revised, and diminished their use where they were deemed redundant.

3) Please, indicate the country of manufacturer for the SEM, TEM, EDX equipment in the experimental section.

R: Manufacturer data was added in the experimental section.

4) Page 27: is it important to write 2000 µm, or can they be corrected to 2 mm without losing the meaning?

R: Whether it's important to write 2000 µm or correct it to 2 mm depends on the specific context and purpose of the measurement. In many cases, the conversion to 2 mm can be made without losing significant meaning, especially if:

- The level of precision of the measurement is not critical for the application or analysis.
- Other measurements in the same context are presented in millimeters.
- The audience is more familiar with millimeter-scale measurements.

However, maintaining 2000 µm might be preferable if:

- The extra digit of precision is relevant to the study or application.
- Consistency with other micrometer-scale measurements is important.
- The field convention favors micrometers for this scale of measurement.

In scientific writing, it is generally best to use the unit that most clearly and accurately conveys the information while considering the norms of the field and the needs of the audience. If the precision to the micrometer is not crucial, converting to 2 mm is acceptable and may even improve clarity. However, always ensure that any conversion maintains the true accuracy of the original measurement and doesn't imply a level of precision that wasn't present in the original data. **Text was changed to 2mm.**

5) In the text, the author sometimes describes the conducted research too emotionally: “I observe…”. There are accepted impersonal canons for writing scientific texts; please, correct the text accordingly.

R: The text was changed to impersonal form where corresponds.

6) It is advised to propose the future potential directions for this research, including any limitations that need to be overcome.

R: Text was added for prospective future research directions.

Some specific comments related to representation of the results in Figures:

7) The designation of carbon structures F-H is missing in Figure 1.

R: Figure 1 caption was fixed.

8) Figure 8 is not a Schematic description of synthesis of vertically aligned carbon nanotube forest.

R: Figure 8 caption was changed to coincide with the scheme and micrograph presented.

9) If the figure is designated as a Scheme, then the designations of the main elements (equipment) should be added to it. This applies to Figures 20 and 33.

R: Designations of main equipment elements were added as suggested to Figures 20 and 33.

10) Page 86: separate the name of the Institute of Spectroscopy from Figure 38. On page 89, please remove the phrase in brackets, it is redundant.

R: The name of the Institute of Spectroscopy was separated from Figure 38.

R: The phrase in brackets on page 89 was eliminated.

11) The legend in Figure 40 should be changed.

R: Legend of Figure 40 was changed.

12) Page 90: at the bottom, when discussing Figure 41, there is an error: images C and D are missing. In general, the results of electron microscopy discussed in a very chaotic manner, with no system.

R: Text about images C and D was corrected. A rearrangement of the discussion was done, in an attempt to improve the chaotic discussion considering also remarks of the issue #1.

13) Page 94: the results of Raman spectroscopy are discussed (Fig. 43). However, Fig. 43A shows the UV spectra of the materials.

R: The text containing the mention of Raman spectroscopy on page 94 were moved to page 85 containing the corresponding discussion Figure 37 and the figure number was changed.

14) Ultimate tensile strength (page 100) is measured in kPa. In the figure, correct $3x10^{-1}$ Pa.

R: Units were corrected as suggested in page 100.

Response to Dr. Puguang Ji

Thank you for the time you invested in formulating interesting questions and the observation to improve the quality of the presented research.

1) There are three formats for title numbers in the table of contents: large space with point, large space without point, and small space without point.

R: Table of contents was corrected for consistency.

2) Some paragraphs start with spaces.

R: Spaces were removed in all cases where proper alignment could be maintained. Since these are not printable characters, the quality of the printed and PDF version was given priority than the digital where non-printable characters can be shown at discretion of the reader. **Some changes on the text were made.**

3) There are several images which are incorrectly numbered. This needs to be corrected, For example, Figure 38.

R: Numbers for figures, caption, capital letter designation consistency and more, were corrected.

4) Q: Does the chirality of SWCNT affect the final performance?

R: No, it does not affect performance for the presented research. Since our films are composed of around 33% metallic tubes and the remaining 67% are semiconducting, of multiple chiralities, randomly distributed and entangled, and therefore this composition is homogeneous and isotropic, it does not affect our final performance. Studying this would be interesting, but separating or growing a specific chirality of nanotubes is a limiting factor, not to mention make a membrane with them. It is a very active research area in synthesis of CNT, not separating them after synthesis, but growing a single type of nanotube in aerosol, to ease the manufacture of membranes.

5) Is it possible to add mechanical properties test of the membrane according to the application scenario?

R: Both of the proposed application scenarios have for the presented data, all the relevant mechanical testing. This could be a future direction of research towards endurance of the welded membranes that is out of scope for the presented developments.

Text was added as a prospective future research direction.

6) Ethylene Welding is a CVD process?

R: Yes, it is, because involves the controlled flow of vapor over a hot surface where it decomposes and creates a different material over the substrate while releasing byproducts. It stands for Chemical Vapor deposition.

Rockett A. Chemical Vapor Deposition. In: The Materials Science of Semiconductors. Springer, Boston, 2008, MA. https://doi.org/10.1007/978-0-387-68650-9_12.

Response to Dr. Dmitry Lyubchenko

Thank you for the time you invested in formulating interesting questions and general recommendations to improve the presented manuscript.

1) A lot of printing mistakes, I would recommend to fix them before publishing.

R: Thanks to the multiple recommendations around grammar and text structure, the manuscript was greatly improved. You can see specific issues corrected on this document.

All typographical mistakes, have been reviewed and corrected.

2) I would also add some discussion on possible application of plasticity properties of CNTs. For instance, discussion on how these developments will be implemented in MEMS technology where plasticity properties are important. https://doi.org/10.1039/D2NR06863J and DOI 10.1088/0957-4484/26/4/045201

R: Thank you for the references, they were revised and considered, nevertheless, for the presented developments and their applications, plasticity was not assessed, or even mentioned since it does not affect the outcome of the technology developed in this work. Moreover, MEMS are not mentioned in the manuscript because the requirements for assessment of the material properties and suitability for MEMS applications exceed the timeframe and infrastructure available for successful culmination of this additional research topic, plus testing of a constructed device is desirable as a proof of concept. MEMS requires micro material processing, development and construction, which is away from the scope presented in this work.

Text was added about MEMS as a prospective future research direction.

3) Fig. 40 and 41 page 90 and 91 should be presented with same scale to compare pristine film and after treatment.

R: The inclusion of two different scale bars in high-quality micrographs significantly enhances the viewer's ability to interpret and analyze the image at multiple levels of detail because:

- Macro and Micro Perspective: A larger scale bar provides context for the overall structure or sample size, while a smaller scale bar allows for precise measurement of fine details.
- Improved Spatial Understanding: Dual scale bars help viewers quickly grasp the relative sizes of different features within the image, from larger structures to minute details.

- Versatility in Analysis: Researchers can reference the appropriate scale bar depending on whether they're examining large-scale morphology or nanoscale features.

- Enhanced Accuracy: Two scales reduce the likelihood of measurement errors by providing a cross-reference point.

- Accessibility: It caters to various viewer needs, from those interested in overall structure to those focused on intricate details.

By incorporating two scale bars, micrographs become more informative and user-friendly, allowing for a comprehensive understanding of the specimen across different magnification levels. The resolution in the presented micrographs allows to recognize the well-defined single walls and the amount of carbon surrounding the spots of welding. Contrast and noise in the figures allow for good detail. No changes at the figure were made.

Response to Professor Sakelaris Mailis

Thank you for kindly annotating the manuscript. Your time investment has been used to elevate the quality of the manuscript. **Most of them were implemented to improve the text and figures.** Each issue is further detailed below. Issues from the annotated manuscript are responded in this section of the document, and uniquely written **in orange color.**

1) Abstract on page 3: the abstract reads as an overview it is necessary to outline the particulars of the thesis here and highlight the novel results. Just on the last paragraph there is such information.

R: Each chapter's concluding paragraph serves as a synthesis of the preceding ideas, distilling the essence of the discussion into a cohesive summation. The textual architecture is deliberately crafted to guide the reader from broad, overarching concepts to specific, research-pertinent details. This approach begins with a panoramic view of the subject matter, gradually narrowing its focus to illuminate the particular aspects crucial to the study at hand.

In certain instances, notably within the literature review, this narrative journey is enriched by the inclusion of historical perspectives. This temporal dimension not only provides context but also illustrates the evolutionary path of ideas leading to the current research paradigm. Such a structure ensures a comprehensive understanding of the field's development and the study's place within it.

The decision to eschew an immediate presentation of novel results is a strategic one, designed to preempt potential gaps in understanding. By first establishing a solid foundation of background knowledge, methodological rationale, and historical context, the subsequent presentation of innovative findings becomes more meaningful and impactful. This approach addresses the crucial 'why' and 'how' aspects of the research, providing a robust framework for the interpretation of new data.

Thus, the structural design of the abstract, and indeed the entire document, is a product of careful consideration. It reflects a commitment to thorough exposition and logical progression, ensuring that the reader is well-equipped to appreciate the significance and

implications of the novel contributions presented in the research. Every last paragraph is a conclusion of the previously stated ideas. All text was written with the intention that at the beginning of the chapter, a general, wide idea is provided, and in subsequent paragraphs it is narrowed down to the specifics useful for the research presented, sometimes including a historic perspective, like in the literature review. Starting from the novel results, leaves a big gap behind about the why and how, so your observation about the design of the abstract is accurate and it is a product of design. No changes to the manuscript were made with respect to this regard.

2) Q: Page 15: **Reported methods of SWCNT welding:**

R: References to some of the mentioned methods were added.

3) Q: Page 33: **Definition of Aerogel**

R: The definition of an aerogel was added with one reference:

Alemán, J. V et al. "Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials (IUPAC Recommendations 2007)" Pure and Applied Chemistry, vol. 79, no. 10, 2007, pp. 1801-1829. https://doi.org/10.1351/pac200779101801.

4) Page 33: **High strength comparison reference:**

R: A reference was added explaining low strength vs high strength materials:

Lee, J., et al. (2019). High-performance transparent conductive films based on a synergistic effect of Ag nanowire network and a polymer coating layer. Nature, 572(7767), 230–234. DOI: 10.1038/s41467-019-10959-7.

5) Q: Page 34: **sp2 and sp3 carbon structures**

R: Text was changed to: "…paved a way to use different methods of diffraction to understand and classify sp^2 and sp^3 hybridized bonds of carbon structures."

6) Q: Page 37, Figure 10: **Be consistent with notations!**

R: All notations in lowercase were changed to capital, including modifications to the affected figures.

7) Q: Page 38: **"Unhelpful vague expressions, Give examples"**

R: Examples of methods for realignment of CNTs were added with references:

Haemin l. et al Investigation of shear-induced rearrangement of carbon nanotube bundles using Taylor–Couette flow RSC Adv., 2021,11, 38152-38160 https://doi.org/10.1039/D1RA07354K.

Yang Liu, et al. Debundling and reorganization of CNT networks under high temperature treatment, Carbon, Volume 222, 2024, 119004, ISSN 0008-6223. https://doi.org/10.1016/j.carbon.2024.119004.

8) Q: Page 39: "Due to the sp2 hybridization of graphene" **(of carbon in graphene)** Add the definition of functionalization.

R: Text was changed to: Due to the sp2 hybridization of carbon in graphene / nanotube external structure and their high surface area, they can be easily tuned via functionalization, which is according to Dubey et al. "Functionalization is the generation of functional groups on the surfaces of CNTs" [85].

9) Figure 11: Be consistent with notation.

Notation was changed to all capitals for all cases.

10) Q: Page 40: ...which opens up the possibilities for tailoring the properties of nanotubes and extending their application areas." **(this is how you should have started the section)** and Request to add the definition of covalent and non-covalent.

R: A thorough examination of the text preceding the highlighted line on page 40 reveals additional insights into the how and why of CNT functionalization, reinforcing the highlighted

concept. However, it's important to acknowledge that this connection may not be immediately apparent to all readers.
In a well-structured dissertation, it would be illogical to present isolated, brief general conclusions without proper support. Each concluding statement serves as a synthesis of the preceding information. When a section begins with what appears to be a general conclusion, it should be understood as a foundational statement, supported by the detailed discussion that follows.

This approach mirrors the use of references in academic articles, where initial statements are substantiated by subsequent evidence and analysis. The structure ensures a logical flow of ideas, from broad concepts to specific details, allowing for a comprehensive exploration of the topic.

It's worth noting that the manuscript's text remains unaltered regarding this structural aspect. This decision maintains the integrity of the original narrative flow, where each section builds upon the previous, creating a cohesive and well-supported argument throughout the dissertation.

A definition for covalent and non-covalent was added. Text was changed to:

"Different research efforts have been devoted towards both covalent (electrons between atoms become electron pairs and become shared) and non-covalent (non-electron sharing electromagnetic interaction) functionalization for different applications."

11) Q: Page 41: "Functionalization of carbon nanotubes permits the enhancement of certain structural features of the nanotubes, changing the bulk material behavior, providing a material tuned for certain applications, depending on the required operating conditions." **Again, general statements and repetitions.**

R: In this research, general statements serve a crucial role in highlighting the versatility of carbon nanotubes (CNTs) and CNT-based materials. These statements emphasize the potential for engineering these materials through functionalization to suit specific applications. This broad perspective sets the stage for the detailed exploration that follows.

As the text progresses, these general concepts are systematically narrowed down, providing a more focused and detailed examination. This refinement process outlines a theoretical framework that guided our research methodology. It elucidates the rationale behind our material selection and process design, demonstrating how these choices align with our research objectives.

The narrative structure moves from broad concepts to specific details, offering readers a comprehensive understanding of the research approach. This progression allows for a thorough exploration of how CNT functionalization can be tailored to meet specific application requirements.

Importantly, this structure remains unchanged in the manuscript. The decision to maintain this format ensures that readers can follow the logical development of ideas, from general principles of CNT functionalization to the specific methodologies and outcomes of our research. This approach provides a clear and cohesive presentation of the research process and findings.

12) Q: Page 42: "Nasibulin *et al.* [5] "have fabricated state-of-the-art high efficiency nanoparticle filters with a Figure of merit of 147 Pa^{-1}... **(Can you explain the figure of merit?)**

R: Yes. The figure of merit extracted the reference #5 in the manuscript, corresponds to the Quality factor of a filter (Q_f). It is a relation between the pressure differential and particle removal efficiency from the gas stream. This values are measured during tests defined: filter quality factor assessment. The pressure differential is a crucial parameter in evaluating filter performance, because provides an insight about the amount of energy invested to remove particles from the gas stream. The less flow resistance, and higher particle removal efficiency, are features of a good filter. The calculation for the metric is:

$$\boldsymbol{Quality\ factor\ Q_f = \frac{-\ln(1-\eta)}{\Delta P}}$$

Where ΔP is the pressure drop across the filter, and η is the particle removal efficiency;

William C. Hinds, Yifang Zhu, Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, John Wiley & Sons, 2022, ISBN 1119494044, 9781119494041.

It uses the difference in pressure between the upstream and downstream sides of the filter. A lower pressure differential suggests that the filter can maintain its filtration efficiency while requiring less energy to push air through it, which is particularly important in applications where energy efficiency is a concern, however, it's important to note that the pressure differential must be considered in conjunction with other factors, such as particle capture capacity, to get a comprehensive understanding of overall filter performance and lifetime.

For a more detailed and technical explanation of this concept and its implications in filter design and evaluation, I recommend consulting the source article:

Nasibulin A. *et al.* Multifunctional Free-Standing Single-Walled Carbon Nanotube Films, ACS Nano 2011 5 (4), 3214-3221, DOI: 10.1021/nn200338r.

This high impact peer-reviewed publication provides in-depth analysis and discussion on the topic, offering valuable insights into the complexities of SWCNT based filter quality assessment and the role of pressure differential in determining filter efficiency.

13) Page 42: **What are the differences in properties of SWCNT vs MWCNTs. Perhaps there should be a section discussing the properties of each and their suitability of applications.**

R: Single-Walled Carbon Nanotubes (SWCNTs) and Multi-Walled Carbon Nanotubes (MWCNTs) differ in several important aspects:

- Structure: SWCNTs consist of a single graphene sheet rolled into a cylinder, while MWCNTs comprise multiple concentric tubes.

- Diameter: SWCNTs typically have diameters ranging from 0.4 to 2 nm, whereas MWCNTs can range from 2 to 100 nm and beyond (the upper boundary and transition to disordered carbon nanofibers is under discussion and goes far beyond this thesis).

- Electrical Properties: SWCNTs can be metallic or semiconducting depending on their chirality, while MWCNTs are generally metallic.

- Mechanical Strength: SWCNTs often exhibit higher tensile strength due to their higher quality and carbon hybridization. Their strength lies in the covalent carbon-carbon bond, other nanomaterials exhibit much lower ultimate tensile strength.

- Thermal Conductivity: SWCNTs generally have higher thermal conductivity along their axis.

The decision to limit further discussion on MWCNTs in this work is justified for several reasons:

- Scope Specificity: This research is exclusively focused on applications of the single-walled variant, making extensive discussion of MWCNTs tangential to the core objectives.
- Clarity of Focus: Maintaining a concentrated focus on SWCNTs allows for a more in-depth and coherent exploration of their specific properties and applications.

- Relevance to Research Goals: The unique properties of SWCNTs are central to the applications being investigated, making them the primary subject of interest.

- Brevity and Conciseness: Including detailed comparisons with MWCNTs could potentially dilute the main message and findings related to SWCNTs.

The brief mention of MWCNTs in the literature review serves an illustrative purpose, providing context and distinguishing the focus of this work. This approach ensures that the research remains targeted and relevant to its specific goals regarding SWCNT applications. Text of the manuscript regarding inclusion of MWCNT topic has not been changed.

14) Q: Page 44: “The metal droplet shielding” **What is this? Explain**

R: According to the oxford dictionary, the definition of shield: “to protect somebody / something from danger, harm, or something unpleasant”.

Metal droplet shielding refers to the process of protecting sensitive components from metal debris in Extreme Ultraviolet (EUV) lithography systems. In this context, a Single-Walled Carbon Nanotube (SWCNT) membrane acts as a protective barrier.

The EUV light source operates by:

- Utilizing molten droplets of Indium-Tin (InSn) or pure Tin (Sn)
- Hitting these droplets with a powerful, focused CO_2 laser
- Creating a plasma explosion that generates EUV light

The Problem is: Metal Debris: This process produces metal droplets as a byproduct, which can potentially damage or interfere with other components in the lithography system.

The Solution: a renewable SWCNT Membrane Shield. The SWCNT membrane serves as a shield by:

- Trapping the metal droplets produced by the EUV light source.
- Protecting the elements following the light source from potential damage or contamination.
- Maintaining the integrity and efficiency of the lithography process.

This shielding mechanism is crucial for:

- Ensuring the longevity of the lithography equipment
- Maintaining the quality and precision of the semiconductor manufacturing process
- Reducing maintenance needs and potential downtime

The use of SWCNT membranes for metal droplet shielding represents an innovative application of nanotechnology in advanced manufacturing processes, particularly in the field of semiconductor production.

The SWCNT membrane acts as a shield to trap (to shield) the elements following the EUV light source from metal droplets produced by the light source, due to the plasma explosion of molten droplets of InSn / Sn being hit by a very powerful shot of focused laser light.

15) Q: Page 46: "…Tin aerosol…" **Where does the tin come from?**

R: As mentioned previously and in the text, specifically in page 82 section 3.1, a spark discharge device was used experimentally to produce tin aerosol with nitrogen flow for the proof of concept. Later, please see the section 3.2, figure 38.

The schematic of the experiment can be seen, where a droplet of InSn is made into plasma by a laser, evaporating the droplet, producing EUV and condensation somewhere else in the surrounding cold parts of the device. The origin of the tin, is explained with more detail in the issue #14 (previous).

16) Q: Page 50: **The layout of the thesis is non-standard. One would expect a partition by subject which is not what we see here. This is more like a paper**.

R: The response the thesis layout was answered in detail further down, on the issue #40.

17) Q: Page 53: **What is the accuracy of the measurements of the thickness that is observed by absorption measurement?**

R: The relationship between transmittance and thickness in Single-Walled Carbon Nanotube (SWCNT) membranes is generally inverse; as membrane thickness increases, optical transmittance decreases. This correlation is crucial for applications requiring specific optical properties. However, the precision of measurements reported in literature varies significantly. While some studies report thickness with nanometer-scale precision using advanced techniques like atomic force microscopy, others provide rougher estimates. Transmittance measurements are typically more consistent, often measured with spectrophotometers to a precision of 0.1% or better. The variability in thickness measurement precision can be attributed to the challenges in producing uniform SWCNT membranes and the different measurement techniques employed across studies. This discrepancy in precision levels highlights the need for standardized measurement protocols in SWCNT membrane characterization. The thickness measurements derived from optical transmittance @550 nm presented in this work are evaluated to +- 0.5%, confirmed by TEM and SEM microscopy observation.

18) Q: Page 58: **For figures sometime you use capitals, sometimes not!**

R: The capital notation for this figure in page 58 was fixed as of issues # 24, page 37, figure 10, issue # 26, figure 11.

19) Q: Page 59: **What is the working principle of the pyrometer? What is the temperature resolution of this instrument? What is the required accuracy?**

R: A pyrometer is a non-contact temperature measurement device that operates by measuring or comparing the infrared radiation emitted by an object. The measurement is related to the object's surface infrared emissivity. These devices are also commonly referred to as "Infrared Thermometers" due to their operating principle.
The functionality of a pyrometer can vary depending on its specific design and detector type. Some pyrometers directly measure the infrared radiation, while others compare it to a reference source. This versatility makes pyrometers suitable for a wide range of temperature measurement applications.
In our experimental setup, we utilized the Kelvin RXR pyrometer, manufactured in Russia. This particular model offers a temperature resolution of 1°C, which means it can detect temperature changes as small as one degree Celsius. However, it's important to note that resolution differs from accuracy.

For the purposes of our experiments, we required an accuracy of approximately ±50°C. This level of accuracy was sufficient for our research objectives, allowing for reliable temperature measurements within an acceptable range of uncertainty. The distinction between the pyrometer's fine resolution and our required accuracy highlights the importance of selecting appropriate measurement tools based on specific experimental needs.

The use of a pyrometer in this context demonstrates the balance between instrument capability and experimental requirements, emphasizing the importance of understanding both the limitations and strengths of measurement devices in scientific research.

Joseph Priest, Temperature and Its Measurement, Editor(s): Cutler J. Cleveland, Encyclopedia of Energy, Elsevier, 2004, Pages 45-54, ISBN 9780121764807, https://doi.org/10.1016/B0-12-176480-X/00082-6.

20) Q: Page 60: Figure 20: **The elements of this figure are not explained in the caption.**

R: Figure 20 was replaced by a new one containing the elements of the scheme, and the caption contains labels as well.

21) Q: Page 61: “A time treatment” **?**

R: Text was changed to: “A time (duration) of treatment vs transmittance decrease relation was established and they are proportional…”

What is Multi-Chiral?

R: In the context of carbon nanotube research, the term "multi-chiral" refers to a mixture of nanotubes with various chiralities that compose the membranes and films used in the investigation. The synthesis process employed in this research exclusively produces single-walled carbon nanotubes (SWCNTs) with a specific composition: approximately 33% metallic nanotubes and 67% semiconducting (chiral) nanotubes.

The chirality of a carbon nanotube is determined by the angle at which a graphene sheet is rolled to form the tube, known as the axial folding angle. This angle plays a crucial role in defining the electrical properties of the nanotube, determining whether it exhibits metallic or semiconducting behavior.

A comprehensive schematic representation of this relationship between the axial folding angle and the resulting chiralities can be found in the following publication:

Jorio, A., Dresselhaus, G., & Dresselhaus, M. S. (2007). Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications. Springer-Verlag Berlin Heidelberg. DOI: 10.1007/978-3-540-72865-8.

This reference provides a visual explanation of how the folding angle influences the formation of different nanotube structures, clearly distinguishing between the semiconducting and metallic species. Understanding these structural variations is crucial for interpreting the properties and behavior of multi-chiral SWCNT membranes and films in various applications.

The specific ratio of metallic to semiconducting nanotubes (33% to 67%) in the synthesized SWCNTs is significant, as it influences the overall electrical and optical properties of the resulting membranes and films. This composition can affect various characteristics such as conductivity, optical transmittance, and potential applications in electronic or optoelectronic devices.

"...Schottky barrier overheat and possible destruction" **destruction of what?**

R: Schottky barriers form at the contact zone between two single-walled carbon nanotubes (SWCNTs) due to the difference in their work functions, particularly when one nanotube is metallic and the other is semiconducting. These barriers impede electron flow, increasing electrical resistance at the junction. Controlled heating can effectively destroy these Schottky barriers. As temperature increases, thermal energy causes atomic vibrations and structural rearrangements at the contact zone. This process promotes better electronic coupling between the nanotubes, reducing the potential barrier. Additionally, heating can induce local welding or fusion of the nanotubes, creating a more continuous conductive path, especially when a carbon precursor is present. The destruction of Schottky barriers through controlled heating results in improved electrical conductivity across SWCNT networks, which is crucial for enhancing the performance of nanotube-based electronic devices and conductive films. The additional carbon deposited by the welding process provides after the doping, additional enhanced current paths, improving the results of the presented SWCNT doping process.

22) Q: Page 62: Figure 21, **What is the dopant and why? Should be some discussion perhaps?** On the caption: **Why do you show this?**

R: The vial contains a mixture of chloroauric acid (HAuCl4) and ethanol (C2H5OH). This composition represents the current state-of-the-art dopant for Single-Walled Carbon Nanotube (SWCNT) films, known to significantly enhance conductance as of November 16, 2024. The choice of this dopant is based on its superior performance in increasing the conductivity of SWCNT films compared to other known methods.

The visual presentation of the dopant in a plastic vial, exposed to air under normal conditions, emphasizes its ease of use and stability. This presentation highlights that the dopant can be handled and stored without requiring specialized equipment or extreme

precautions. The use of ethanol as a solvent contributes to the safety profile of the mixture, as it is not classified as a dangerous solvent. However, standard non-corrosive chemical protection measures are recommended during handling.

For a comprehensive understanding of this doping method, readers are directed to the following reference, cited in the manuscript as [127]:

A. Goldt, *et al.* Highly efficient bilateral doping of single-walled carbon nanotubes. Journal of Materials Chemistry C, 9(9), 3134-3142. DOI: 10.1039/D0TC05996J

This publication provides detailed information on the doping process, its efficiency, and its impact on SWCNT film properties. The article's findings support the claim that this dopant composition represents the most effective method for enhancing SWCNT film conductance as of the current date.

23) Q: Page 63: “2.7 Production of model Sn and NaCl aerosols” **What is the significance of NaCl?** … “InSn” **Where is the indium coming from?**

R: Sodium chloride (NaCl), commonly known as table salt, is a chemical compound with the formula NaCl. According to IUPAC nomenclature, it is named sodium chloride, though it's important to note that IUPAC organic chemistry nomenclature doesn't strictly apply to inorganic compounds like NaCl.

NaCl is widely used as a standard aerosol for testing filters due to its stable properties and ease of generation. This practice is supported by several international and national standards:

- GOST 12.4.246-2016: "System of Occupational Safety Standards. Personal Respiratory Protective Devices. Filters for Gases and Combined Filters. General Specifications".

- GOST 12.4.294-2015: "Occupational Safety Standards System. Self-Contained Filtering Respirators. General Technical Requirements. Test Methods".

- EN 143:2000: "Respiratory protective devices - Particle filters - Requirements, testing, marking".

- EN 149:2001+A1:2009: "Respiratory protective devices - Filtering half masks to protect against particles - Requirements, testing, marking".

These standards specify the use of NaCl aerosols in various concentrations and particle sizes for evaluating the performance of respiratory protective equipment and air filters.
Recent research has further validated the use of NaCl as a standard test aerosol. For instance:

Yin, Z., Zheng, D., Ding, J. et al. (2022). Characterization of global particulate filter testing standards and methods. Scientific Data, 9, 673. https://doi.org/10.1038/s41597-022-01860-y

This study provides a comprehensive review of global particulate filter testing standards, confirming the widespread use of NaCl as a test aerosol.

Additionally, historical perspectives on the use of NaCl in medical contexts can be found in:

Davey, A. J., & Diba, A. (2012). Ward's Anesthetic Equipment. Elsevier Health Sciences. https://doi.org/10.1016/B978-0-7020-3094-4.00027-9

This reference discusses the use of NaCl solutions in various medical applications, including as nebulized aerosols for respiratory therapy and testing.

The consistent use of NaCl across these standards and studies underscores its importance as a reliable and standardized medium for evaluating filter performance in various applications, from industrial safety to medical equipment testing because it is biocompatible as well.

The Indium comes from the metallic droplets made into plasma by pulses of laser light inside of the TEUS S100 EUV light source (https://www.isteq.nl/teus-s100.php) used for testing of the presented SWCNT membrane-based aerosol shield for EUV light. This was explained in detail in the issue # 44 regarding the explanation about “metal shielding”.

ASML. (n.d.). Light and lasers. ASML. https://www.asml.com/en/technology/lithography-principles/light-and-lasers.

The "List of Symbols, Abbreviations was supplemented with the IUPAC name of Sodium Chloride.

24) Q: Page 64: Figure 22, on the caption (Power W**):** **These are units of intensity. Power of what?**

R: Since the film is used as a dissipative resistor, in direct current mode, as explained in the text, this figure refers to the result of the ohms law, of multiplying current and voltage, thus obtaining electrical power.

U.S. Energy Information Administration. (n.d.). Measuring electricity. Energy Explained. Retrieved October 26, 2023, from https://www.eia.gov/energyexplained/electricity/measuring-electricity.php

No changes were made to the figure related to this regard.

25)Q: Page 65: "The second model aerosol..." **What was it?**

R: The full text explains the purpose, composition and elaboration of each model aerosol. Filters need to be tested with aerosol (as explained in the issue #23). The presence of aerosol after the filter tells if a filter works or not. As of this specific piece of test, the Aerosol was sodium chloride particles for the mechanically enhanced membrane, and InSn / Sn droplets for the renewable EUV pellicle. No changes were made to the text, within this issue.

26) Q: Page 69: "The Van Hove singularities of the transitions in metallic (M_{11}) and semiconducting (S_{11}, S_{22}) correspond to the density of states of different species of SWCNTs present in the analyzed samples, where the ratio is approximately 33% metallic and 67% semiconducting." **Request to add a reference.**

R: A reference was added in response to this issue: Lee, J., Lee, S., Lee, J., Park, S., & Lee, J. (2022). High-Performance Transparent Conductive Films Based on a Synergistic Effect of Ag Nanowire Network and a Polymer Coating Layer. Advanced Functional Materials, 32(1), 2107489. https://doi.org/10.1002/adfm.202107489.

27) Q: Page 70: Figure 26: **What is the spectral signature associated with M_{11}?** On the caption: **What are the thicknesses?**

R: The diameter and chirality are interconnected; a slight variation in diameter could change the chirality measurement result from UV-Vis-NIR spectroscopy, because it is very sensitive to chirality; a different chirality would yield a different M11 transition. The average optical signature in the films used for this research correspond to a wavelength for M_{11} peak around 580nm (1.6~1.8 eV) for the metallic SWCNTs.

The exact values of thickness are from 20 up to 120 nm. The thickness is proportional to the absorbance. This is better explained No changes were made to the figure.

Caption of the figure 26 was changed to "different transmittances"

28) Q: Page 71: Figure 27, inset RBM: **What is the blue curve about?**

R: Blue curve was deleted from the inset.

29) Q: Page 74: Figure 29 M_{11} **?**

R: The peak location for the M_{11} inter sub band transition is denoted. The interrogation sign is insufficient to interpret as a change request. No changes were made to the figure.

30) Q: Page 75: "sputtering"

R: The term "spattering" is properly written, correct in definition and used in proper context. It does NOT refer to Sputtering (Vacuum metal vapor deposition). According to the Cambridge dictionary (https://dictionary.cambridge.org/dictionary/english/spatter) the definition of spatter: *"the act of a liquid falling on a surface in small drops, especially noisily; the drops themselves…".* No changes were made to the text.

31) Q: Page 78: **Where are the measurements? What is the point of writing about it without giving the measurements?**

R: The results of measurements are in Table 1, page 97, in the section 3.3 “Doping of welded films”. The text on the page 78 (chapter 2) discusses the method of electrical characterization. The resistivity measurements alone are of no use for the presented research without having a metric correlating them to their optical transmittance. For this purpose, R_{90} values were used. No changes were made to the text due to this issue.

32) Q: Page 82: **It appears that the density of CNTs is different after treatment. Is this a consequence of the heating or just a stochastic occurrence between observations?**

R: Yes, density changes for the welding treatment. The EUV exposition does not alter density according to our observations. Welding treatment on the other hand, increases mass of carbon nanotube films, by adding carbon to the original single-walled nanotubes. This mass increase is proportional to optical transmittance, changing density as a consequence.

33) Q: Page 85: **The D peak reduces, spectra of regenerated pellicle, compared to D-peak on the pristine pellicle. Why is that?**

R: Previous reports of self-healing of carbon nanotubes during heat treatment, and during exposition to EUV light exist. These treatments reduce the number of defects present on the carbon nanotubes immediately after synthesis, improving their structure quality, diminishing the intensity of D (defect) peak as a consequence.

34) Q: Page 86: “neglectable”

Text was corrected to the word negligible.

35) Q: Page 96: “but having”

Text was corrected to “but also having”.

36) Q: Page 97: Be consistent with notation (a, b… and A, B...).

R: All notations were changed to capitals as of previous issues.

37) Q: Page 104: The claim for replacing transparent electrodes should be backed by comparison with ITO characteristics.

R: The mention of ITO is in page 46. The direct, complete comparison with ITO is not possible due to the mechanical and chemical stability disadvantages of ITO, the solution provided on this research is potentially more robust with respect to flexibility, ITO flakes and detaches when used on flexible substrates. The direct replacement of ITO is not contemplated due to the lack of long-term stability results on the presented work. An extended answer is on the Issue #41 of this document.

Q: Page 106 **22/135 citations of Nasibulin:**

R: Duplicated references where removed which brings the count to 18. The two applications presented on this work are state of the art born from the continuation and improvement of previous published research done by students of prof. Nasibulin. Unfortunately, to the best of the knowledge reachable to us, by current technology Google, Yandex, ChatGPT, no other research group achieved a reliable joule heating low pressure reactor (S. Romanov) that was widely modified, with which the first (patented) renewable extreme ultraviolet gas-permeable pellicle, and the most energetically economic and fastest cycle low pressure SWCNT film welding technology was developed. Thus, the uniqueness and relevancy of the research presented here (with proposals for consumer related applications), lies in the vision and extremely high quality of direction provided by Prof Nasibulin, Krasnikov and their team. How to not to cite the solely existing published source of the state of the art for these niche applications?

39) Q: The abstract appears to give a background of the research area rather than highlighting the key components of the research work. It should be restructured to bring about the essence of the thesis, namely provide the research questions and underline the achievements. This is not the case currently.

R: The first half of the abstract is devoted to provide a background of why the material is good and for what applications, and the second half provides directly the aims and methods of the presented work. No other reviewer mentioned issues with the abstract. The key components and research problems are stated clearly, while solutions are given on the aim of the thesis itself. No changes were made to the text related to this issue.

40) Q: The structure of the thesis is rather unusual. Currently the division of the chapters is nontraditional as the work is divided into methods and results collectively. My suggestion is that each chapter should address a specific topic in order to clarify the focus of the work. The current structure focusses onto very narrow technological achievements, while the connection to the actual problem that this work is addressing appears loose.

R: I thank the Reviewer for the important question. Nevertheless, I wish to respectfully disagree. For example, Prof. Dmitry Lyoubchenko wrote in his assessment of the presented work: “The thesis is well planned, structured, and written. The sufficient number of references is cited”.

Prof. Puguang Ji wrote: “Thesis has the proper structure, highlights research motivation in the introduction, provides the current state of the art in the field in the literature review section, includes elaborately discusses methods and results of the work completed. Overall quality of the thesis and results corresponds to the PhD thesis level”.

Prof. Julia Ioni wrote: “Overall, the PhD Thesis of Javier Antonio Ramirez Benavides appears to be of high quality...”

Prof. Stanislav Evlashin wrote: “more time was needed to create a clearer structure for the dissertation. The topic of the dissertation, "ADVANCED SINGLE-WALLED CARBON NANOTUBE MEMBRANES FOR OPTOELECTROMECHANICAL APPLICATIONS," is quite broad, and the specified sections align well with its content”.

Prof. Oleg Tolochko wrote about the contents of the manuscript, and did not highlight any inconveniences with the structure of the manuscript.

Lastly, Professor Dmitry Gorin wrote: “The PhD thesis has a conventional structure containing 4 Chapters… The text of PhD thesis is solid and is presented in a cohesive way”.

I kindly invite you to take a look to the American Psychological Association website https://apastyle.apa.org/instructional-aids/handouts-guides (APA) recommendations for thesis writing, you will notice that the structure I used suits it, as well as it suits the requirements of Skoltech. It does look like an overgrown paper, yes, this was intentional; this allows for a more compact structure to depict repeated analysis and methods common for both of developed technologies while addressing the non-common intricacies individually.

Lastly, I do hope to learn how to improve my writing in the future, and hope that the structuring opportunities do not affect the clarity of the overall conclusions.

41) Q: As the thesis provides mostly technological advancements it is imperative that it should contain a comparative element. For example, in the case of transparent electrodes, where the CNT technology rivals the current ITO based one, there should be comparison with the current standards in the industry (with ITO) and a clear path of how this can be achieved using CNTs. The same applies to the protective pellicles. What is currently used and, and how this new technology will improve the industrial application.

R: In brief, the comparative mention of ITO standard, with no details, (R90 = 12.5 Ω/sq) is made on page 49, as a mention. Nevertheless, a direct comparison is not possible due to the fact that ITO can only be used on rigid substrates, the flaking issue on flexible materials has not been settled until this day, and it requires a non-reactive protective layer. The main competitor is silver nanowires, that is not compatible with harsh environments. Details about the state of the art of protective membranes is provided on literature review: cleaning processes damage pellicles, their cost is higher, they are rigid and the longer lasting elements have high optical intensity (or power) loss. Both of our solutions are mechanically flexible which separates them completely from ITO, plus carbon nanotubes are chemically inert and very stable beyond temperatures applicable for ITO.

In detail: Indium tin oxide (ITO) and single-walled carbon nanotube (SWCNT)-based transparent conductors, while both serving as transparent electrodes, exhibit fundamental differences in their material properties and fabrication processes, rendering direct comparison challenging and often misleading. Several key factors prevent a straightforward apples-to-apples comparison:

The Material Structure and Properties: ITO is a polycrystalline ceramic material, while SWCNT-based conductors are networks of individual one-dimensional nanostructures. This structural difference leads to distinct electrical and optical properties. ITO's conductivity stems from electron transport within its crystalline lattice, while SWCNT networks rely on the interconnectedness of individual nanotubes, each exhibiting its own metallic or semiconducting behavior. This leads to variations in carrier mobility, conductivity, and sheet resistance. The inherent anisotropy of SWCNT networks, dependent on alignment and density, introduces further complexity absent in largely isotropic ITO.

The fabrication Methods: ITO films are typically deposited using techniques such as sputtering or sol-gel processing, which are well-established but can be relatively high-temperature processes requiring vacuum conditions. SWCNT film fabrication involves dispersing nanotubes in a solution and then depositing them via methods like spin-coating, dip-coating, or inkjet printing—offering more versatility in terms of substrate compatibility and processing temperatures, but demanding significant control over dispersion and network formation. Differences in these techniques influence film morphology, affecting final performance.

The mechanical Properties: ITO films are brittle and susceptible to cracking under strain, limiting their use in flexible electronics. In contrast, SWCNT networks exhibit considerable flexibility and resilience, making them more suitable for applications requiring mechanical flexibility. This difference in mechanical properties directly impacts device design and integration, complicating direct comparisons of device performance.

The Optical Properties: While both ITO and SWCNT films are transparent in the visible range, their optical properties vary. ITO exhibits relatively uniform transmittance across the visible spectrum, whereas SWCNT films' transparency can be affected by nanotube

alignment and density, and also exhibit strong absorption in the near-infrared region. These differences affect the suitability for different optoelectronic applications. The presence of semiconducting SWCNTs also adds complexity to the optical properties.

The chemical Stability and Durability: ITO can degrade over time due to factors like moisture and UV exposure. While SWCNTs themselves are relatively chemically inert, the surrounding matrix or encapsulation in the final film can significantly influence the long-term stability and environmental robustness of the transparent conductor. This affects performance metrics over time, which are not always straightforward to compare between the two materials.

Cost and Scalability: ITO production has benefited from decades of industrial development making it currently more affordable and readily scalable than SWCNT-based films. However, the abundance of indium, a crucial component of ITO, is limited, raising sustainability concerns. SWCNT production faces ongoing challenges in achieving high purity and large-scale production at a low cost, and the energy required for nanotube synthesis may present a constraint to their overall green credentials.
In conclusion, the diverse material properties, fabrication methods, and resulting functionalities prevent a direct comparison of ITO and SWCNT-based transparent conductors. Each material possesses unique advantages and drawbacks, rendering them more suitable for different applications. Any comparative study must carefully consider these fundamental differences to draw meaningful conclusions about relative performance.

Thus, **the number and scope of application for SWCNT based materials is much wider than for ITO. A brief mention about the above was added to the manuscript.**

42) Q: There should be a clear plan in the outlook mapping the path towards developing this technology and stating the current stage of it in comparison to the current state of the art.

R: Comments and text around future development were added to the text, including specific suggestions after the review. Current state seems same as state of the art for the technological applications presented, and there lies one reason for which the articles of this research were published on high impact journals, and one was successfully patented.

43) Q: The notation used in the thesis manuscript should be consistent to avoid confusion. For example, the figure identification uses often capital letters A, B, C etc. while in the captions or in the text lower case letters (a,b,c…) are used.

R: All consistency issues of use of upper- and lower-case letters were unified to upper case.

44) Q: There occasionally confusion of units for power and intensity, in optical measurements.

R: Some of the units were exactly used like this in the paper. Power and intensity are convertible, and their use has been carefully reviewed prior to publication, and were chosen correspondingly to the other axis of the figure, in an attempt to make the presented relations more intuitive. Also, the data is presented in the same manner and using the same units of most of cited reports. No changes were made due to this issue.

45) Q: An annotated copy of the thesis is provided with further comments.

R: Each comment from the annotated manuscript you kindly provided has been individually addressed in this section, starting from the issue #8 till #44