

TALLINN UNIVERSITY OF TECHNOLOGY
DOCTORAL THESIS
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**Development of Silicon Oxynitride
Nanocomposites with Single-Walled
Carbon Nanotubes as Protective Coatings
for Solar Cells**

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Author's contribution to the publications

Contribution to the papers in this thesis are:

- I Deposition of PHPS films, search for optimal curing parameters, measurement of UV-Vis and FTIR spectra, XPS data fitting, interpretation and visualization of the UV-Vis, FTIR, XPS, SEM, SEM EDX and line-scan results, author performed major part of writing in cooperation with co-authors.
- II Fabrication of SiO_xN_y /SWCNT composites, measurement of UV-Vis, FTIR and Raman spectra, interpretation and visualization of the UV-Vis, FTIR, Raman, SEM, SEM EDX results, author performed major part of writing in cooperation with co-authors.
- III Fabrication of SiO_xN_y /SWCNT composites, measurement of UV-Vis, FTIR and Raman spectra, performing the scratch tests, interpretation and visualization of the UV-Vis, FTIR, Raman, SEM, SEM EDX, SE results, author performed major part of writing in cooperation with co-authors.

Introduction

A number of very serious challenges, ever increasing due to the impact of human activity on the environment and climate, have prompted discussions about the need to switch to alternative energy sources [1]. In addition to reducing environmental impacts, this transition is important in terms of growing population and economic growth, which drive an increased demand for energy, especially since fossil fuels are a finite source of energy [2]. It is projected that by 2050, 39% of global electricity production will come from renewable sources [3]. The current situation in Europe clearly illustrates the need for more serious actions aimed at developing new technologies and improving existing ones [4].

Photovoltaic (PV) energy, produced from an infinite and widely available source – solar radiation, is a promising alternative to energy from fossil fuels [5]. The strong increase in fossil fuel prices for energy production in recent years, the unfavorable global economic situation, and the increasing commercialization of solar cells (SC) have led to a significant reduction in the cost of PV technologies, which makes their use even more attractive. [6]. However, environmental factors are critically affecting the performance and lifetime of SCs [7]. In this regard the reliable and efficient technology of glass inflexible encapsulation for SCs has become widely used. But, the high weight (at least 2/3 of the total weight of the solar panel) and inflexibility significantly limit the use of standard glass protection for SCs, especially for modern flexible devices. In recent years, numerous attempts have been made to replace cover glass with other types of protection, mainly with polymer-based materials [8]. This task is challenging, as such coatings must meet all functional requirements i.e. excellent barrier protection against gases, humidity and ultraviolet (UV) irradiation, mechanical protection and often flexibility, chemical and thermal stability, etc., and, at the same time, the fabrication technology must be low-temperature, dependable, scalable, and inexpensive. Therefore, the selection of optimal protection is promising from both a technical and economic point of view, which is especially important nowadays.

Pre-ceramic polymer perhydropolysilazane (PHPS) is a promising candidate to be an encapsulant material due to its capabilities to transform/cure into vitreous SiO_xN_y films using relatively simple technologies avoiding the use of vacuum and high-energy waste processes. Diluted in organic solvents, this pre-ceramic material combines the process ability of liquid polymers and the high functional properties of resulting ceramics (glasses), and it also offers potential scalability of the technological process. Currently, PHPS-derived SiO_xN_y films are actively used as encapsulant coatings, such as for SCs and microelectronics, due to their high barrier (against oxygen, water and UV irradiation), dielectric, and anti-corrosion properties, as well as their non-toxicity and high thermal and chemical stability [9,10]. The high optical transmittance of PHPS-derived films makes them promising for optical applications [11].

However, there are some disadvantages. Despite the outstanding barrier properties reported in the literature, the long-term stability of PHPS-derived SiO_xN_y films raises questions, as it has not been well studied. Additionally, due to their inorganic nature, PHPS-derived films exhibit high mechanical hardness but relatively poor ductility. This effect became increasingly pronounced with an increase in the film thickness, starting from 250 nm and leading to brittle fracture of the material, which limits its use in the manufacture of flexible devices. [12]. One experimentally proven way to increase the flexibility of PHPS-derived layers is the strategy of alternating them with layers of more flexible (organic) materials. This results in a multilayer protective coating, but this leads

to problems with adhesion (peeling) of the layers during operation [9,12]. Therefore, composite technology looks promising as another alternative option that has not yet been widely explored, as the choice of different fillers allows for significant tuning of the properties of the resulting SiO_xN_y /filler composite films.

Possessing a high elastic modulus and extremely high strength, carbon nanotubes (CNTs) have established themselves as a promising reinforcing filler material in a number of different matrices such as polymers, ceramics, etc. They can also influence the matrix's thermal and structural properties [13,14]. Moreover, the alignment or orientation of CNTs within a matrix material gives possibility to prepare composite films with predictable anisotropy of coatings properties [15]. It should be noted that such composites based on PHPS-derived films with CNTs have not yet been studied.

Thus, the main focus of this doctoral thesis was to improve the state-of-the-art SiO_xN_y protective coatings derived from PHPS by combining them with CNTs. During this work, a simple and scalable process for the formation of protective nanocomposite coatings with oriented CNTs was developed. For the first time, the structural and functional properties of such composites were studied and described, and the effect of optical antireflection was found and investigated. In addition, several knowledge gaps regarding filler-free PHPS-derived films were addressed. Extensive work was conducted to compare the influence of two different low-temperature curing methods of PHPS on the structure and functional properties of the resulting SiO_xN_y coatings. For the first time, the optical constants of PHPS-derived films were measured and compared, and a study of the long-term stability of the composition and properties of prepared coatings was conducted. It was found that the PHPS-based coatings developed and investigated during the project could be promising for a wide range of other applications, not limited to the protection of flexible SCs.

The doctoral thesis is based on three publications and structurally consists of three chapters. The first chapter is a literature review that provides an overview of existing PV technologies, discussing their structure and the factors affecting their stability and operation. Special attention is given to device encapsulation approaches and the materials used for this purpose, leading to the consideration of PHPS as an alternative protective material for thin-film encapsulation. This chapter also describes the structure and properties of PHPS, the methods of its transformation/curing into SiO_xN_y , and an overview of successful strategies for the application of PHPS-derived SiO_xN_y films in PV and other fields. In addition, the chapter discusses objective disadvantages, which may be possible to overcome by creating a nanocomposite SiO_xN_y /filler coating with embedded and oriented CNTs as a filler.

Chapter 2 provides detailed information about the materials and methods used to prepare the samples and to characterize the properties of the SiO_xN_y /CNT composite coatings and SiO_xN_y matrix films that are the subject of this thesis. Chapter 3, which contains the main results and their discussion, is divided into two sections. The first section focuses on the study and comparison of the structure and properties of filler-free PHPS-derived matrix films cured by two different low-temperature methods. The second section is entirely devoted to the formation and characterization of SiO_xN_y /CNT composite films. Each of these sections is divided into subsections based on the subject of discussion.

The results obtained during the work on this thesis were presented as poster and oral presentations at several Estonian and international conferences from 2021 to 2024. They were also published as three peer-reviewed articles on which this thesis is based.

Abbreviations and symbols

Δ	Phase difference of reflected light
Δn	Difference between refractive indices
A, B, C, and D	Material coefficients in the Cauchy dispersion formulas
AFM	Atomic force microscopy
a-Si	Amorphous silicon
CdTe	Cadmium telluride
CNTs	Carbon nanotubes
COF	Coefficient of friction
CS	Cross-section
CVD	Chemical vapor deposition
d	Thickness
EDX	Energy dispersive X-ray spectroscopy
EU	European Union
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infrared spectroscopy
k	Absorption index
L_c	Critical load
MWCNTs	Multi-walled carbon nanotubes
n	Refractive index
PCE	Power conversion efficiency
PET	Polyethylene terephthalate
PHPS	Perhydropolysilazane
PSZ	Polysilazane
PV	Photovoltaic
PVF	Polyvinyl fluoride
R^2	Correlation parameter between measured and calculated SE data
RBM	Radial breathing mode
r_p	Fresnel reflection coefficient for p-polarization state
r_s	Fresnel reflection coefficient for s-polarization state
RT	Room temperature
SCs	Solar cells
SE	Spectroscopic ellipsometry
SEM	Scanning electron microscopy
SLG	Soda lime glass
SWCNTs	Single-walled carbon nanotubes
$\tan \psi$	Ratio of the reflection coefficients for different light polarizations

1 Literature review

1.1 Photovoltaics as one of the most promising alternative energy sources

The importance of switching from traditional to alternative energy sources has been discussed for a long time. This discussion was motivated by the need to address the complex problem of the sustainable development of humanity [16]. This problem is associated with the increasingly harmful impact of human activities on the environment, which subsequently threatens the entire ecosystem of the planet. Transitioning to environmentally sustainable development is one of the major goals of the recent agenda of European Union (EU) policymakers. The European Commission has developed its environmental policy under the European Green Deal, which aims to achieve climate neutrality of the EU by 2050 [17,18].

To achieve these goals, comprehensive work is being conducted to change established processes in the economic, industrial, agricultural, transportation, energy, and other related fields. All measures taken in various sectors aim to build a circular economy. This economy optimizes the consumption of resources, organizes their recycling and reuse, while simultaneously reducing emissions of harmful gases into the atmosphere and minimizing the disposal of waste into landfills [19,20]. An aspect that is inextricably linked to all of the above is energy use. The use of fossil fuels to generate electricity is a catalyst for the rapid increase in greenhouse gas emissions into the atmosphere [21]. Besides influencing climate factors, it also affects the environment. Statistics show that about 75% of EU greenhouse gas emissions come from energy use and production. This is why the change of energy sources is one of the most important steps towards a climate-neutral EU [17].

A reduction in emissions can be achieved by switching to renewable or green energy sources [7,22]. The variety of events in recent years and their impact on the EU energy sector clearly illustrated the need for more serious actions aimed at developing new technologies and improving existing ones [4,6].

Photovoltaics (PV) is developing rapidly and now is the third largest renewable energy source after hydroelectric power and wind power, and it has the greatest potential due to its universal geographical availability [23–26]. The source of electricity for PV is electromagnetic radiation, which most often comes from the sun but is not limited to it, thus becoming an abandoned and an inexhaustible source. The tool for this conversion is special semiconductor devices called solar cells (SCs).

Given these factors, the intensive development of solar power generators is becoming increasingly important in many areas of the economy, including energy, construction, agriculture, transportation, and aviation. In recent years, the production of SCs has become increasingly cost-effective, leading to their increasingly widespread use.

1.1.1 Types and structure of solar cells

Solar cells consist of multiple layers of different materials that perform specific functions to ensure the successful conversion of photons into electrical energy over the long term.

The entire volume of developed solar cells is usually divided into three generations according to the architecture and type of material used for photon absorption.

First-generation SCs include devices based on mono- and polycrystalline silicon wafers, which have the highest certified power conversion efficiency among currently

this layer over the same period of time [40]. Controlling the optical properties of solar cells by adding antireflective coatings or patterns increases the penetration of solar radiation into the device [36,41].

As can be seen from the above, when trying to move away from the traditional inflexible glass technology of solar cell protection, significant difficulties arise in finding alternative and flexible materials. Silicon-based materials appear to be the most promising option currently being explored for encapsulating flexible and sensitive SCs of the third-generation. Among silicon-based materials, polysilazanes can be singled out separately. These precursors allow the production of carbon-free (inorganic) glass-like flexible coatings and appear to be a promising candidate for the role of an alternative to classical encapsulation glass.

1.2 Polysilazanes as potential encapsulating materials

Polysilazane (PSZ) is a close relative of siloxanes and is also being tested as an encapsulant for SCs. PSZ belongs to the group of special preceramic silicon-based polymers (Figure 1.5) with a Si–N–Si backbone, including various reactive or inert side groups at the Si and N atom sites [42,43]. PSZs are called preceramic because the result of transformation of the polymer precursor under certain conditions is ceramics. PSZs most commonly used in liquid form as solution in organic solvents.

These polymers have received much attention from science and industry in recent decades due to their wide range of attractive functional properties and corresponding applications. Due to their chemical structure and reactivity, PSZs are beneficial for chemical functionalization, allowing for the tuning of material properties [44,45]. Additionally, to achieve the goal of adjusting properties if this is the task, PSZs are often used as components for the formation of hybrid or composite materials [46].

PSZs can be used to form ceramic fibers, which can then be used as reinforcing materials in various composites [47]. However, the dominant application area for PSZs is in formation of coatings and thin films.

embedding of a small amount of nanofiller [77]. Nowadays, based on the goals of sustainable development, great attention is paid to the development of cost-effective and highly functional composites [78].

In general, a composite consists of a matrix material and filler materials that can be introduced into the matrix in various ways. Glass, ceramics, and metals are most often used as matrices, but polymers have become truly widespread [76,79,80]. The filler is usually either fibers, which are more in the micrometer range, or various forms of nanostructures [76].

In most cases, composites are created to improve the mechanical properties of the matrix, but the areas of application are not limited to this [81]. With the active development of nanomaterials, the possibilities of using composites extend to electronics, optics, sensors, and PVs [15,82–84]. For example, one strategy for improving the encapsulation of SCs using EVA is the introduction of various fillers into the polymer matrix, which positively affects the protective properties and long-term stability of the composite material [8].

Composites with nanocarbon materials as fillers are especially popular due to the wide range of unique properties of carbon allotropic forms [79,80]. Among the nanocarbon allotropes, there are different dimensional forms: diamond (3D), graphite (2D), graphene (1D), and fullerene (0D) [85]. In addition to the dimensions, they differ in hybridization of carbon atoms and their volume distribution, which determines the properties of the material. Graphene is one atomic layer of graphite. Carbon nanotubes (CNTs) are also one of these forms. They are classified as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), which are one or many seamlessly rolled sheets of graphene, respectively [86].

The use of CNTs to enhance the mechanical stability or thermal management of polymers has been intensively explored and confirmed [87–89]. In this regard, CNTs are a promising candidate for the role of filler to improve the mechanical and flexible properties of PHPS-derived films.

1.3.1 CNTs as a filler for creating a PSZ-based composite coating

Active research into carbon nanotubes began in the 1990s and continues to the present day. Like any nanoparticle, CNTs can be synthesized using top-down and bottom-top methods. Arc discharge, chemical vapor deposition (CVD), and laser ablation methods are traditionally used for synthesis. Depending on the chosen method, different sources of carbon and energy are required for the synthesis of CNTs [77,90,91].

As mentioned above, nanotubes can be obtained by rolling a graphene sheet into a cylinder along the lattice vector of the graphene plane. The number of rolled graphene sheets determines the number of nanotube walls. The choice of vector determines the diameter and chirality of the tubes. The diameter of the tubes is in the nanometer range, while their length can reach hundreds of micrometers. The vector also affects whether the nanotubes display metallic or semiconductor properties [86,92,93].

It should be noted that the SiO_xN_y coatings are insulators, which can contribute to the accumulation of electrostatic charge, potentially leading to damage of the PV module as a result of discharge. In this regard, embedding a conductive filler such as CNTs can help mitigate this issue.

CNTs have outstanding optical and mechanical properties, as well as high thermal conductivity [90,94]. All these properties are directly related to the chemical bonds in the network of carbon atoms, that is, the backbone of the CNTs. These properties are

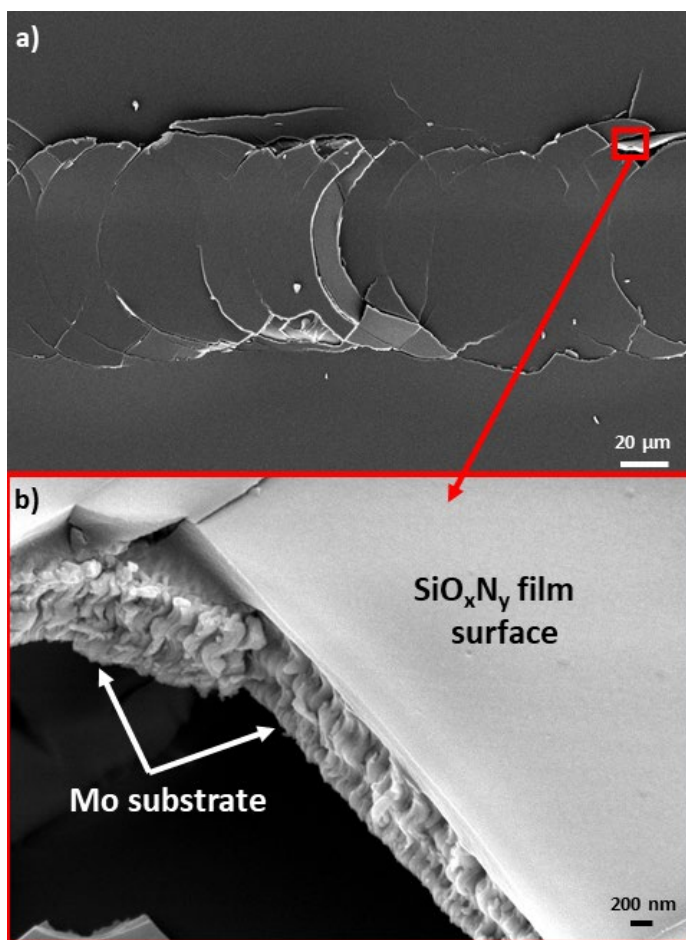


Figure 3.11. SEM images of UV-cured sample: (a) a fracture of a scratch on an SiO_xN_y matrix film under high load (near the end of the scratch), and (b) a magnified image of one of the fragments.

This difference in the behavior of 1-day-aged films was also associated with their CS structure after curing. The plasticity and lack of hardness of fresh thermally cured films were associated with the absence of a top layer of silicon dioxide and the presence of a very high nitrogen content throughout the film thickness. As a result of aging and ripening, the nitrogen content in the film decreased, and a layer similar in composition to silicon dioxide appeared on the surface. These changes made the aged film more comparable to the UV-cured samples.

For all samples, the coefficient of friction (COF) values did not exceed an average of 0.05. Such low COF values indicated the high smoothness of the film surface. The high smoothness of the film surfaces was also confirmed by the atomic force microscopy (AFM) results. The average surface roughness of the UV-cured and thermally annealed SiO_xN_y films was around 0.6 nm. Figure 3.12 shows COF curves for some samples. For all samples, the same behavior was observed for the COF value, depending on the scratching time.

cured samples using SEM (Figure 3.14). For both TOP and BOTTOM architecture, the surface of the cured samples was mainly uniform, without any noticeable pores. Only under very high magnification was it possible to see some inhomogeneity points, with its minor presence on the film surface. The CS micrographs showed that in the case of the TOP architecture, the composite film thickness was around 400 nm and the SWCNT layer was predominantly located in the upper part of the SiO_xN_y matrix, not penetrating into its depth. For the BOTTOM configuration, the film thickness was 480 nm, with the SWCNT film layer predominantly located in the bottom part of the SiO_xN_y matrix. It should be noted that in both cases, the SWCNT film continued to be densely packed in cross-section after entering into the coating matrix. When the sample was fractured to create a cross-section, the SWCNTs were stretched and torn. These fragments could be seen emerging from the film in the images, illustrating the additional bonding effect of SWCNT fillers inside the composite film.

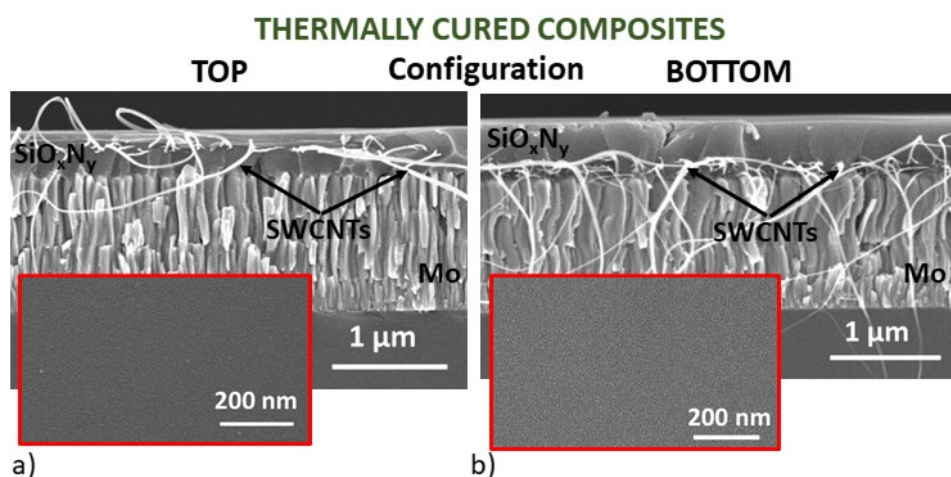


Figure 3.14. SEM cross-sectional and surface (in the red frame) images of SiO_xN_y /SWCNT composite films on SLG/Mo substrates with architecture (a) TOP and (b) BOTTOM.

The surface of UV-cured SiO_xN_y /SWCNT composite films on SLG/MO substrate (Figure 3.15a and d) appeared the same as that of the thermally cured ones. In the CS (Figure 3.15b, c, e), the SWCNT distribution within the matrix showed the trends observed for thermally cured composite samples. However, in the case of the TOP configuration, SWCNTs were predominantly located in the upper layers of the SiO_xN_y matrix film but might shift and spread deeper, moving from the laminated structure of the composite to a network (Figure 3.15b and Article III). This behavior could be due to the diffusion of stressed SWCNTs in viscous matrix material. During UV-induced curing, the film was gradually cured starting from the surface downward, allowing the SWCNTs to remain longer in the viscous, uncured matrix film, which could lead to their spreading throughout the volume of the matrix film.

References

1. Pastuszak, J.; Węgierek, P. Photovoltaic Cell Generations and Current Research Directions for Their Development. *Materials* **2022**, *15*, 5542, doi:10.3390/MA15165542.
2. Sorrell, S. Reducing Energy Demand: A Review of Issues, Challenges and Approaches. *Renewable and Sustainable Energy Reviews* **2015**, *47*, 74–82, doi:10.1016/J.RSER.2015.03.002.
3. Bhattacharya, M.; Paramati, S.R.; Ozturk, I.; Bhattacharya, S. The Effect of Renewable Energy Consumption on Economic Growth: Evidence from Top 38 Countries. *Applied Energy* **2016**, *162*, 733–741, doi:10.1016/J.APENERGY.2015.10.104.
4. Adedoyin, F.F.; Erum, N.; Taşkin, D.; Chebab, D. Energy Policy Simulation in Times of Crisis: Revisiting the Impact of Renewable and Non-Renewable Energy Production on Environmental Quality in Germany. *Energy Reports* **2023**, *9*, 4749–4762, doi:10.1016/J.EGYR.2023.03.120.
5. Li, X.; Li, P.; Wu, Z.; Luo, D.; Yu, H.-Y.; Lu, Z.-H. Review and Perspective of Materials for Flexible Solar Cells. *Materials Reports: Energy* **2021**, *1*, 100001, doi:10.1016/J.MATRE.2020.09.001.
6. Gajdzik, B.; Wolniak, R.; Nagaj, R.; Žuromskaitė-Nagaj, B.; Grebski, W.W. The Influence of the Global Energy Crisis on Energy Efficiency: A Comprehensive Analysis. *Energies* **2024**, *17*, 947, doi:10.3390/EN17040947.
7. Wu, M.; Ma, B.; Li, S.; Han, J.; Zhao, W. Powering the Future: A Critical Review of Research Progress in Enhancing Stability of High-Efficiency Organic Solar Cells. *Advanced Functional Materials* **2023**, *33*, 2305445, doi:10.1002/ADFM.202305445.
8. Gaddam, S.K.; Pothu, R.; Boddula, R. Advanced Polymer Encapsulates for Photovoltaic Devices – A Review. *Journal of Materiomics* **2021**, *7*, 920–928, doi:10.1016/J.JMAT.2021.04.004.
9. Kim, D.; Jeon, G.G.; Kim, J.H.; Kim, J.; Park, N. Design of a Flexible Thin-Film Encapsulant with Sandwich Structures of Perhydropolysilazane Layers. *ACS Applied Materials & Interfaces* **2022**, *14*, 34678–34685, doi:10.1021/acsami.2c06699.
10. Back, H.S.; Kim, M.J.; Baek, J.J.; Kim, D.H.; Shin, G.; Choi, K.H.; Cho, J.H. Intense-Pulsed-UV-Converted Perhydropolysilazane Gate Dielectrics for Organic Field-Effect Transistors and Logic Gates. *RSC Advances* **2019**, *9*, 3169–3175, doi:10.1039/C8RA09831J.
11. Baek, J.J.; Park, S.M.; Kim, Y.R.; Chang, K.C.; Heo, Y.-J.; Bae, G.Y.; Choi, K.H.; Shin, G. Intense Pulsed UV Light Treatment to Design Functional Optical Films from Perhydropolysilazane: An Alternative to Conventional Heat Treatment Processes. *Journal of Materials Science* **2022**, *57*, 254–273, doi:10.1007/S10853-021-06598-3.
12. Channa, I.A.; Distler, A.; Zaiser, M.; Brabec, C.J.; Egelhaaf, H.-J. Thin Film Encapsulation of Organic Solar Cells by Direct Deposition of Polysilazanes from Solution. *Advanced Energy Materials* **2019**, *9*, 1900598, doi:10.1002/AENM.201900598.
13. Arash, B.; Wang, Q.; Varadan, V.K. Mechanical Properties of Carbon Nanotube/Polymer Composites. *Scientific Reports* **2014**, *4*, 6479, doi:10.1038/srep06479.

28. Pscherer, M.; Günthner, M.; Kaufmann, C.A.; Rahm, A.; Motz, G. Thin-Film Silazane/Alumina High Emissivity Double Layer Coatings for Flexible Cu(In,Ga)Se₂ Solar Cells. *Solar Energy Materials and Solar Cells* **2015**, *132*, 296–302, doi:10.1016/J.SOLMAT.2014.09.015.
29. Prajapat, K.; Mahajan, U.; Kumar, A.; Dhonde, M.; Sahu, K.; Vyas, S.; Riyad, Y.M.; El-Bahy, Z.M. Next-Generation Counter Electrodes for Dye-Sensitized Solar Cells: A Comprehensive Overview. *Sustainable Materials and Technologies* **2024**, *42*, e01178, doi:10.1016/J.SUSMAT.2024.E01178.
30. Maani, T.; Celik, I.; Heben, M.J.; Ellingson, R.J.; Apul, D. Environmental Impacts of Recycling Crystalline Silicon (c-Si) and Cadmium Telluride (CDTE) Solar Panels. *Science of The Total Environment* **2020**, *735*, 138827, doi:10.1016/J.SCITOTENV.2020.138827.
31. Tao, J.; Yu, S. Review on Feasible Recycling Pathways and Technologies of Solar Photovoltaic Modules. *Solar Energy Materials and Solar Cells* **2015**, *141*, 108–124, doi:10.1016/J.SOLMAT.2015.05.005.
32. Chen, X.; Xu, G.; Zeng, G.; Gu, H.; Chen, H.; Xu, H.; Yao, H.; Li, Y.; Hou, J.; Li, Y. Realizing Ultrahigh Mechanical Flexibility and >15% Efficiency of Flexible Organic Solar Cells via a “Welding” Flexible Transparent Electrode. *Advanced Materials* **2020**, *32*, 1908478, doi:10.1002/ADMA.201908478.
33. Ma, S.; Yuan, G.; Zhang, Y.; Yang, N.; Li, Y.; Chen, Q. Development of Encapsulation Strategies towards the Commercialization of Perovskite Solar Cells. *Energy & Environmental Science* **2022**, *15*, 13–55, doi:10.1039/D1EE02882K.
34. Wang, T.; Yang, J.; Cao, Q.; Pu, X.; Li, Y.; Chen, H.; Zhao, J.; Zhang, Y.; Chen, X.; Li, X. Room Temperature Nondestructive Encapsulation via Self-Crosslinked Fluorosilicone Polymer Enables Damp Heat-Stable Sustainable Perovskite Solar Cells. *Nature Communications* **2023**, *14*, 1342, doi:10.1038/s41467-023-36918-x.
35. Kauk-Kuusik, M.; Li, X.; Pilvet, M.; Timmo, K.; Grossberg, M.; Raadik, T.; Danilson, M.; Mikli, V.; Altosaar, M.; Krustok, J.; Raudoja, J. Study of Cu₂CdGeSe₄ Monograin Powders Synthesized by Molten Salt Method for Photovoltaic Applications. *Thin Solid Films* **2018**, *666*, 15–19, doi:10.1016/J.TSF.2018.09.025.
36. Aitola, K.; Sonai, G.G.; Markkanen, M.; Kaschuk, J.J.; Hou, X.; Miettunen, K.; Lund, P.D. Encapsulation of Commercial and Emerging Solar Cells with Focus on Perovskite Solar Cells. *Solar Energy* **2022**, *237*, 264–283, doi:10.1016/J.SOLENER.2022.03.060.
37. Rolston, N.; Printz, A.D.; Hilt, F.; Hovish, M.Q.; Brüning, K.; Tassone, C.J.; Dauskardt, R.H. Improved Stability and Efficiency of Perovskite Solar Cells with Submicron Flexible Barrier Films Deposited in Air. *Journal of Materials Chemistry A* **2017**, *5*, 22975–22983, doi:10.1039/C7TA09178H.
38. Dong, Q.; Liu, F.; Wong, M.K.; Tam, H.W.; Djurišić, A.B.; Ng, A.; Surya, C.; Chan, W.K.; Ng, A.M.C. Encapsulation of Perovskite Solar Cells for High Humidity Conditions. *ChemSusChem* **2016**, *9*, 2597–2603, doi:10.1002/SSC.201600868.
39. Ma, S.; Yuan, G.; Zhang, Y.; Yang, N.; Li, Y.; Chen, Q. Development of Encapsulation Strategies towards the Commercialization of Perovskite Solar Cells. *Energy & Environmental Science* **2022**, *15*, 13–55, doi:10.1039/D1EE02882K.
40. Li, Y.; Huang, X.; Ding, K.; Sheriff, H.K.M., Jr.; Ye, L.; Liu, H.; Li, C.-Z.; Ade, H.; Forrest, S.R. Non-Fullerene Acceptor Organic Photovoltaics with Intrinsic Operational Lifetimes over 30 Years. *Nature Communications* **2021**, *12*, 5419, doi:10.1038/s41467-021-25718-w.

54. Prager, L.; Dierdorf, A.; Liebe, H.; Naumov, S.; Stojanović, S.; Heller, R.; Wennrich, L.; Buchmeiser, M.R. Conversion of Perhydropolysilazane into a SiO_x Network Triggered by Vacuum Ultraviolet Irradiation: Access to Flexible, Transparent Barrier Coatings. *Chemistry – A European Journal* **2007**, *13*, 8522–8529, doi:10.1002/CHEM.200700351.
55. Bauer, F.; Decker, U.; Dierdorf, A.; Ernst, H.; Heller, R.; Liebe, H.; Mehnert, R. Preparation of Moisture Curable Polysilazane Coatings: Part I. Elucidation of Low Temperature Curing Kinetics by FT-IR Spectroscopy. *Progress in Organic Coatings* **2005**, *53*, 183–190, doi:10.1016/j.porgcoat.2005.02.006.
56. Dargère, N.; Bounor-Legaré, V.; Boisson, F.; Cassagnau, P.; Martin, G.; Sonntag, P.; Garois, N. Hydridosilazanes Hydrolysis-Condensation Reactions Studied by ¹H and ²⁹Si Liquid NMR Spectroscopy. *Journal of Sol-Gel Science and Technology* **2012**, *62*, 389–396, doi:10.1007/S10971-012-2738-2.
57. Kubo, T.; Kozuka, H. Conversion of Perhydropolysilazane-to-Silica Thin Films by Exposure to Vapor from Aqueous Ammonia at Room Temperature. *Journal of the Ceramic Society of Japan* **2006**, *114*, 517–523, doi:10.2109/jcersj.114.517.
58. Lee, J.-S.; Oh, J.-H.; Moon, S.-W.; Sul, W.-S.; Kim, S.-D. A Technique for Converting Perhydropolysilazane to SiO_x at Low Temperature. *Electrochemical and Solid-State Letters* **2010**, *13*, H23–H25, doi:10.1149/1.3264092.
59. Kozuka, H.; Nakajima, K.; Uchiyama, H. Superior Properties of Silica Thin Films Prepared from Perhydropolysilazane Solutions at Room Temperature in Comparison with Conventional Alkoxide-Derived Silica Gel Films. *ACS Applied Materials & Interfaces* **2013**, *5*, 8329–8336, doi:10.1021/am400845y.
60. Morlier, A.; Cros, S.; Garandet, J.-P.; Alberola, N. Thin Gas-Barrier Silica Layers from Perhydropolysilazane Obtained through Low Temperature Curings: A Comparative Study. *Thin Solid Films* **2012**, *524*, 62–66, doi:10.1016/J.TSF.2012.09.065.
61. Kim, S.-D.; Ko, P.-S.; Park, K.-S. Perhydropolysilazane Spin-on Dielectrics for Inter-Layer-Dielectric Applications of Sub-30 nm Silicon Technology. *Semiconductor Science and Technology* **2013**, *28*, 035008, doi:10.1088/0268-1242/28/3/035008.
62. Riffard, F.; Joannet, E.; Buscail, H.; Rolland, R.; Perrier, S. Beneficial Effect of a Pre-Ceramic Polymer Coating on the Protection at 900 °C of a Commercial AISI 304 Stainless Steel. *Oxidation of Metals* **2017**, *88*, 211–220, doi:10.1007/S11085-016-9705-1.
63. Wang, K.; Günthner, M.; Motz, G.; Flinn, B.D.; Bordia, R.K. Control of Surface Energy of Silicon Oxynitride Films. *Langmuir* **2013**, *29*, 2889–2896, doi:10.1021/LA304307Y.
64. Yang, N.; Wang, W.; Cai, W.; Lu, K. Corrosion and Tribocorrosion Mitigation of Perhydropolysilazane-Derived Coatings on Low Carbon Steel. *Corrosion Science* **2020**, *177*, 108946, doi:10.1016/J.CORSCI.2020.108946.
65. Günthner, M.; Wang, K.; Bordia, R.K.; Motz, G. Conversion Behaviour and Resulting Mechanical Properties of Polysilazane-Based Coatings. *Journal of the European Ceramic Society* **2012**, *32*, 1883–1892, doi:10.1016/J.JEURCERAMSOC.2011.09.005.
66. Prager, L.; Helmstedt, U.; Herrnberger, H.; Kahle, O.; Kita, F.; Münch, M.; Pender, A.; Prager, A.; Gerlach, J.W.; Stasiak, M. Photochemical Approach to High-Barrier Films for the Encapsulation of Flexible Laminary Electronic Devices. *Thin Solid Films* **2014**, *570*, 87–95, doi:10.1016/J.TSF.2014.09.014.

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siirdeala lähedal. Küpsemisprotsessi käigus näitasid mõlemal meetodil kõvendatud SiO_xN_y kihid murdumisnäitaja langust SiO_2 -le omistatavate väärtuste suunas ning UV-kõvendatud proovide ristlõikes esinenud murdumisnäitaja gradient kadus. Seega saab kõiki uuritud kilesid potentsiaalselt kasutada lairiba peegeldusvastaste kattekihtidena mitmesuguste optiliste materjalide jaoks, mille murdumisnäitaja väärtus on üle 1,5.

Leiti, et sadestatud katete adhesiivsed omadused ja nende käitumine mehaanilise mõju all sõltuvad kriitiliselt ka kõvendusmeetodist. UV-kõvendatud maatrikskiled ja SiO_xN_y /SWCNT komposiidid näitasid kõrget kõvadust ja suurepärast adhesiooni SLG/Mo aluspinnaga, säilitades need omadused ka vananemisprotsessi käigus. Termiliselt kõvendatud SiO_xN_y kiled näitasid nõrka adhesiooni SLG/Mo aluspinnaga, madalamat kõvadust ja kõrget plastilisust. Kuid nädal pärast kõvendamist muutus kilede käitumine sarnaseks UV-kõvendatud proovidega, suurendades kriitilise koormuse taluvusväärtust 3 korda. SWCNT-de lisamine SiO_xN_y maatriksisse tugevdas materjali struktuuri ning parandas komposiitkatte vastupidavust purunemisele.

Käesolevas töös valmistati ja uuriti esmakordselt PHPS-st tuletatud horisontaalselt orienteeritud SWCNT täiteainega klaasjaid SiO_xN_y komposiitkatteid. Tõestati tugev seos PHPS-i kõvendusmeetodi ja saadud kilede koostise, morfoloogia, optiliste ja mehaaniliste omaduste vahel. Leiti, et PHPS-i muutmisel ülikindlaks kaitsekatteks on UV-kiirgusega kõvendamise meetod võrreldes termilise kõvendamisega efektiivsem ja sobivam. Optiliste omaduste kohta saadud andmed näitavad, et SiO_xN_y maatrikskiled ja SiO_xN_y /SWCNT komposiidid võivad toimida lairiba peegeldusvastaste katetena. Kõikidel kõvendatud kiledel oli madal hõõrdeteguri väärtus, mis võib olla kasulik rakendustes, kus kriimustuskaitse ja määrimine/libisemine on kriitilise tähtsusega. Saadud tulemused näitavad, et nanotäiteainetega PHPS-maatrikskiledel põhinevad komposiitkatted omavad suurt potentsiaali edasiste teaduslike uuringute ja praktiliste rakenduste jaoks.

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Publikatsioonide loend

1. E.G. Shmagina, E.A. Konshina, D.P. Shcherbinin, P.D. Khavlyuk & M.S. Stepanova, "Photoluminescence enhancement of carbon dots by Ag nanoparticles in thin-film hybrid structures", *Surface Engineering* (2020), DOI: 10.1080/02670844.2020.1747015
2. E. Shmagina, M. Danilson, V. Mikli, S. Bereznev, Comparative study of perhydropolysilazane protective films, *Surf. Eng.* 38 (2022) 769–777, <https://doi.org/10.1080/02670844.2022.2155445>.
3. E. Shmagina, O. Volobujeva, A.G. Nasibulin, S. Bereznev, Fabrication of novel SiOxNy/SWCNT laminate-type composite protective coating using low-temperature approach, *Ceram. Int.* 50 (2024) 34312–34320, <https://doi.org/10.1016/j.ceramint.2024.06.250>.
4. E. Shmagina, M. Antonov, A. Kasikov, O. Volobujeva, E.M. Khabushev, T. Kallio, S. Bereznev, Structural, Mechanical, and Optical Properties of Laminate-Type Thin Film SWCNT/SiOxNy Composites, *Nanomaterials* 14 (2024) 1806, <https://doi.org/10.3390/nano14221806>