REVIEW

by Prof. Tsvetanka Krumova Babeva, PhD, Institute of Optical Materials and Technologies "Acad. J. Malinowski" – Bulgarian Academy of Sciences

of a doctoral thesis for the award of the educational and scientific degree "Doctor", Professional Field 4.1 Physical Sciences, Doctoral Program "Electrical, magnetic and optical properties of condensed matter"

Author: Nikolay Diyanov Minev

Title: Synthesis of nanolayers of 2D materials for applications in optoelectronics

Scientific Supervisor: Prof. Vera Marinova Gospodinova, DSc

1. General description of the submitted materials

The set of materials submitted by Nikolay Minev (in paper and electronic form) contains: an application to the Scientific Council of IOMT for opening a defense procedure; doctoral thesis; extended abstract of the thesis in Bulgarian and English; curriculum vitae in European format; diploma for the educational qualification degree "Master"; list, full-text and summaries in Bulgarian and English of the publications included in the thesis; report on compliance with the minimum national requirements and those of IOMT; declarations of originality and authenticity of the thesis signed by the doctoral student and his supervisor; list of citations; list of projects; additional materials including conference certificates and records of completed training and passed examinations in electron microscopy and spectroscopic techniques for analysis.

The submitted documents comply with the Regulations on the Conditions and Procedure for Acquiring Scientific Degrees and Occupying Academic Positions at IOMT–BAS and are arranged clearly and precisely, which makes a very good impression and demonstrates the doctoral student's serious attitude toward the procedure.

2. Brief biographical information about the doctoral student

During the period 2014–2018, Nikolay Minev was a student at the Faculty of Physics of Sofia University "St. Kliment Ohridski", major "Theoretical Physics", where in 2018 he obtained the educational qualification degree "Bachelor". In the same year, he began his studies in the Master's Program in Medical Physics at the Faculty of Physics of Sofia University. In 2021 he obtained the educational qualification degree "Master" with an excellent grade from the defense of his diploma thesis, developed at IOMT under the supervision of Prof. DSc Vera Marinova. At the beginning of 2022 he started full-time doctoral studies at IOMT and was enrolled with the right to defend in November 2024, one month before the expiration of the three-year term.

Nikolay Minev joined IOMT in September as a Physics Technician. In 2021, he was promoted to the position of Physicist (Higher Education Specialist), and since 2025 he has held the position of Assistant Researcher at IOMT.

Assistant Minev is a co-author of 21 publications indexed in *Scopus* and *Web of Science* (WoS). He has 40 independent citations and an *h*-index of 4. He has participated in the research teams of 8 projects funded by the Bulgarian National Science Fund, the Horizon 2020 Program, the Operational Program "Science and Education for Smart Growth" (OPSESG), and the National Program for Research, Innovation and Digitalization for Intelligent Transformation (PNIIDIT), 5 of which are currently ongoing. He has also participated in 7 projects (3 ongoing) under bilateral cooperation schemes funded by the Bulgarian Academy of Sciences. The results of his work have been presented in 48 poster and oral presentations at international conferences in Bulgaria and abroad, either personally or by co-authors of the respective contributions.

3. Relevance of the research topic

Research on transition metal dichalcogenides (TMDCs, *Transition Metal Dichalcogenides*) is among the most actively developing areas in contemporary materials science, and interest in these materials is continuously increasing. The reason for this is their unique properties, which reveal broad possibilities for application. These materials are considered alternative to silicon, which is reaching its technological limits, and they surpass the well-known and extensively studied graphene because, unlike it, they possess a band gap.

The research in the thesis is focused on noble-metal dichalcogenides, specifically $PtSe_2$, $PtTe_2$ and $PdSe_2$. These materials exhibit good stability when exposed to air, which is an extremely important prerequisite for their application in real devices. Since the properties of these materials depend critically on the number of atomic layers, obtaining monolayers and uniform thickness is of essential importance.

Other challenges in the synthesis process are defects in the crystal lattice and stoichiometry. In this context, the objective of identifying optimal conditions for the reproducible synthesis of $PtSe_2$, $PtTe_2$, and $PdSe_2$ using chemical vapor deposition (CVD) and thermally assisted conversion, investigating the obtained materials, and exploring their potential applications in optoelectronics, is highly relevant, challenging, and strategically important for the advancement of 2D materials.

4 Characteristics and evaluation of the thesis and its extended abstract

The thesis under review consists of an introduction, relevance, objective and tasks, five chapters, conclusion, scientific contributions of the thesis and bibliography. The thesis also includes lists of four publications included into the thesis, twenty participations in scientific conferences and forums and seven research projects related to the thesis topic, as well as eleven citations of the thesis-related publications. Lists of tables and figures, along with the principal symbols and abbreviations used throughout the thesis, are also provided. The work is written in a volume of 160 pages, cites 271 literature sources, the results are illustrated with 55 figures and summarized in 7 tables.

The *first chapter* of the thesis is a review chapter. It describes in general two-dimensional (2D) materials and provides an overview of their properties and applications. Special attention is given to noble-metal dichalcogenides, which constitute the main subject of the thesis. The *second chapter* discusses the principal methods for the preparation and synthesis of transition metal dichalcogenides, as well as the precursors and substrates employed in their fabrication. The *third chapter* is devoted to the characterization techniques used in the thesis. A critical analysis of the applicability of each method is presented, together with its respective advantages and limitations.

The *fourth chapter* describes the preparation of the materials, the optimization of the fabrication protocols, and the characterization of the deposited samples using advanced analytical techniques, including Raman and photoelectron spectroscopy, optical, atomic force and electron microscopy, X-ray and electron diffraction and spectroscopic ellipsometry. The thermally assisted conversion (TAC) method was employed for the synthesis of $PtSe_2$ and $PtTe_2$ samples. The platinum layer was deposited using two different approaches: magnetron sputtering at three deposition times, resulting in platinum selenide/telluride films of different thicknesses after selenization/tellurization, and spin coating of solutions containing liquid platinum precursors. Palladium and platinum selenides were also synthesized by chemical vapor deposition (CVD), with various process parameters systematically varied in order to determine the optimal growth conditions. Atomic force microscopy was used to investigate the influence of the substrate-to-precursor distance on the thickness and surface roughness of the deposited layers. The resulting gradient dependences can be utilized to control the thickness and properties of the deposited materials. High-quality bulk single crystals of orthorhombic $PdSe_2$ were grown using the high-temperature solution growth method, with selenium serving as the solvent.

The fifth chapter of the thesis demonstrates three potential applications of TMDCs, accompanied by comparisons with conventionally used materials. The applications investigated include the use of $PtSe_2$ as a transparent electrode in polymer-dispersed liquid crystal (PDLC) switches, as an antibacterial coating against *Escherichia coli*, and the use of mechanically exfoliated flakes from a bulk $PdSe_2$ crystal in a field-effect transistor (FET). The latter device was fabricated using a dry-transfer technique for the exfoliated flakes. The advantages of employing TMDCs as passive or active media in the investigated applications are clearly demonstrated. In the case of $PtSe_2$ used as an antibacterial coating, additional electron paramagnetic resonance (EPR) analyses were performed to confirm or decline the proposed hypotheses regarding the nature of the antibacterial effect.

In summary, the thesis is written in a clear and concise manner and employs precise scientific terminology. It is very well illustrated. The reader is introduced to the subject matter in a gradual and logical way; each study is well motivated, the obtained results are thoroughly interpreted, and wherever possible, comparisons with the existing literature are provided. A particularly positive impression is created by the summaries provided at the end of each chapter, which are concise, well synthesized, and very easy to understand. The scientific contributions are formulated very well and accurately reflect the results achieved. All of the above demonstrates the thorough understanding of the subject matter from the PhD student and his creative interpretation of the material and the results, as well as the strong commitment and valuable guidance provided by his supervisor.

The thesis abstract accurately reflects the content of the dissertation. It is prepared in accordance with the applicable requirements and is presented in both Bulgarian and English.

5. Scientific contributions and significance of the doctoral thesis

The main scientific contributions of the doctoral thesis can be formulated as follows:

- An efficient method for the synthesis of nanoscale $PtSe_2$ and $PtTe_2$ layers via thermally assisted conversion (TAC) at atmospheric pressure on amorphous substrates has been developed. It has been demonstrated that the process enables precise thickness control and complete conversion of the Pt precursor without residual metallic phase. Structural analyses confirm the formation of a trigonal polycrystalline phase with a predominant crystallite orientation parallel to the substrate. It has been found that continuous $PtSe_2$ coatings are achieved at thicknesses above 9 nm, whereas thinner layers exhibit island-like morphology. It is also shown that the substrate influences the growth mechanism, with vertical growth being promoted on TEM grids. Raman spectroscopy and spectroscopic ellipsometry reveal a well-defined dependence of the vibrational and optical properties on layer thickness, including an increase in the optical band gap with decreasing thickness.
- Recipes for the synthesis of $PtSe_2$ and $PdSe_2$ via the CVD method have been developed, as well as protocols enabling reproducible deposition of platinum dichalcogenides on a wide variety of substrates using a liquid platinum precursor. A flux method has been successfully applied for the growth of high-quality bulk single crystals of $PdSe_2$ with an orthorhombic structure.
- The potential of $PtSe_2$-based PDLC structures for use as light switches in the near-infrared region has been demonstrated. Although the device performance is comparable to that of devices using ITO, $PtSe_2$ layers offer higher transparency in the infrared region. Compared to graphene (another widely studied transparent electrode material), $PtSe_2$ can be directly deposited on flexible substrates without the need for transfer processes, which represents a significant technological advantage.
- A field-effect transistor (FET) was fabricated via a so-called "dry" transfer method, involving precise positioning of mechanically exfoliated flakes obtained from synthesized bulk $PdSe_2$ crystals. The device demonstrates good electrical conductivity, photosensitivity, and environmental stability.

- A high antibacterial activity of $PtSe_2$ layers against *Escherichia coli* has been demonstrated, both in the dark and under UV irradiation. After 6 hours of exposure, the bacterial viability decreased to 1.2%.

I assessed the thesis's contributions as significant and up-to-date within the field of materials science, and in particular within condensed matter physics. They are of both fundamental and applied character and result from thorough and well-focused research work. The fact that the four publications included in the thesis have already been cited 11 times provides additional evidence of the scientific impact and value of the obtained results.

6. Personal impression

I have known Nikolay Minev since 2021, when he joined IOMT. He is an enthusiastic young scientist with a strong inclination toward experimental work, who is interested in new developments, reads extensively, generates ideas, and applies them in practice. I have no doubt that his contribution to the obtained results is substantial.

7. Amendments / questions / recommendations

I have the following questions, which I have arranged in the order in which they appear in the thesis:

- During the optimization of the recipes for obtaining the layers, what were the ranges in which temperature, time, and gas flow were varied, and in what combinations? Were any mathematical models used for experimental design?
- What is the surface roughness of the bare substrates (glass, silicon and quartz) shown in Fig. 21a?
- How were the errors of the parameters in Table 2 calculated?
- What is the stoichiometry of the $PtSe_2$ layers obtained via the CVD method?
- How were the values of V_{th} and V_{sat} determined for 1064 nm (the values in the dissertation text do not correspond to those in Figure 48)? How were the response times in Table 5 determined? What does a response time of 3–50 ms mean?
- Figure 54 – it can be seen that the antibacterial activity increases with thickness. What considerations led to the decision not to use layers thicker than 12 nm? Were any experiments performed under illumination in the visible spectral range?

I have the following comments/recommendations: Page 46 – the sentence related to the determination of the optical band gap should be clarified; E_g is used to denote two different quantities – the optical band gap and the Raman mode; In Figs. 33b and 38b (temperature profile of the process), the initial substrate temperature and the Se temperature during the first 40 minutes are indicated as 0 °C, whereas they correspond to room temperature; Fig. 36 is incorrect – it can be seen from the figure that both thickness and surface roughness increase with distance, whereas the AFM-derived dependencies show the opposite trend, i.e., both parameters decrease with distance; Table 6 – it would be preferable if the presented values for resistance, mobility, etc. were discussed in the main text.

I would like to emphasize that the questions raised and the comments made in no way affect my excellent evaluation of the dissertation, which, as noted above, I consider to be of a very high scientific level.

CONCLUSION

The presented thesis is a completed and significant scientific study with clearly formulated aims and objectives, an appropriately selected and consistently applied research approach, and substantial scientific and applied contributions. The presented results are convincing, well justified, and demonstrate the doctoral candidate's knowledge, ability for creative interpretation, and excellent experimental training. The materials and results presented do not raise any doubts regarding the presence of plagiarism. The dissertation meets the requirements of the Act on the Development of the Academic Staff in the Republic of Bulgaria and the relevant regulations for its implementation for the acquisition of the educational and scientific degree "Doctor". Taking into account the above, **I give my positive assessment** and confidently recommend to the esteemed Scientific Jury **to award** Nikolay Diyanov Minev the educational and scientific degree "Doctor" in the professional field 4.1 Physical Sciences, doctoral program "Electrical, Magnetic and Optical Properties of Condensed Matter".

June 1st 2026

Reviewer:.................................

/Prof. Tsvetanka Babeva, PhD/