Opponent Review of Doctoral Dissertation

Applicant: Mgr. ZUZANA KOŠELOVÁ

Title of Dissertation: DEPOSITION OF FUNCTIONAL OXIDE THIN FILMS TO IMPROVE THE PERFORMANCE OF ELECTRON SOURCES

Opponent: dr hab. inż. Michał Krysztof

Opponent's Department: Department of Microsystems, Faculty of Electronics, Photonics and Microsystems, Wroclaw University of Science and Technology

In accordance with the Study and Examination Rules of BUT, in his/her review the opponent will mainly comment on:
a) the topicality of the dissertation,
b) whether the dissertation achieved its given objective,
c) the problem-solving procedure and the results of the dissertation along with the concrete contribution of the doctoral student,
d) the significance for practical application or the progress in the field,
e) formal and language qualities of the dissertation,
f) whether the dissertation fulfils the conditions of Section 47 (4) of the Act,
g) whether the student proved his/her creative abilities in the given research field and whether the work does or does not comply with the standard requirements placed on the dissertations in the given field. The review is not valid without this conclusion.
It is necessary to add a concise commentary to each of the points below.

Ad a) Topicality of the dissertation

The topic of the dissertation is very topical.
Comment: The topic of developing new field emitters for applications in vacuum micro- and nanoelectronics is very current. The topic of emitter fabrication has been under development for many years and, in the current era of development of vacuum nanoelectronics, is once again gaining relevance. The proposed coating of tungsten emitters with an oxide layer is a very interesting approach to electron beam modelling through the use of a potential barrier, which limits beam energy dispersion and also affects the long-term operation of the emitter by protecting it from bombardment by residual gas ions. The research conducted by the doctoral student may contribute to the development of emitters that can operate in low vacuum conditions, which is essential in some solutions, for example, in the production of mass spectrometers with electron beam ionization.

Ad b) Objective of the dissertation

The objective of the dissertation was achieved.
Comment: The author of the work outlines the objective of the work in great detail in the second chapter, where, in addition to the general outline of the work's purpose, she lists individual specific objectives, including: Optimization of Tungsten Tip Fabrication, Fabrication of Dielectric Tungsten Oxide Coatings, Material Characterization of Coated layers, Analysis of Field Emission Performance, etc.. All of these objectives were achieved to a greater or lesser extent in the course of her PhD studies. The work includes a very extensive and detailed material analysis of both the applied layers and the surfaces of the cleaned substrates and tungsten tips using many research techniques. It also presents an analysis of the performance of selected field emitters, both in terms of emission characteristics and long-term stability. All aspects, including the technology of tip production, the method of cleaning substrates and tips, the methods of applying oxide layers, and the operation of emitters, are discussed in a comprehensive and comparative manner.

Ad c) Problem-solving procedure and the results of the dissertation and the concrete contribution of the doctoral student

The problem-solving procedure and the results of the dissertation are excellent.
Comment: Problem-solving is a strong point for the doctoral student, which is clearly emphasized in the thesis. The presented work is a technological project that requires a systematic approach to work and creative problem-solving during its implementation. Using a set of specialized research techniques, the author can diagnose the problem, describe it, and find a solution or optimize the approach to achieve the intended result. She also takes a creative approach to field emission measurements. Analysing various theoretical aspects of field emission, she selected the most appropriate method to measure and verify the performance of the emitters she fabricated using computer simulations. A very detailed analysis of tungsten oxide fabrication techniques and the potential for their use as passivation layers in the fabrication of field emitters is provided. The author is aware that layers fabricated on flat substrates can differ when the same parameters are used to fabricate layers on tungsten tips, allowing her to adapt the developed procedures and correctly fabricate oxide layers on the emitters. All this demonstrates the author's excellent research skills and merits the title of Ph.D.

Ad d) Significance for practical application or progress in the field

The significance for practical application or progress in the field is excellent.
Comment: The results of this doctoral thesis are significant in the field of vacuum nanoelectronics, which requires the generation of electron beams with specific properties at the microscale using field emitters. They also contribute to the development of analytical techniques using electron beams, such as electron microscopy, where low-energy electron beams would reduce chromatic aberrations in electron lenses, resulting in improved microscope resolution. Atomic force microscopy, where measurements in atmospheric environments would be possible without the need to place the scanning tunnelling microscope in a vacuum chamber, is also important in the context of using analytical methods to characterize the surfaces of thin oxide layers, particularly on tungsten tips. The author describes

procedures that will enable scientists to conduct similar research in the future and characterize further field emitter solutions with dielectric layers.

Ad e) Formal and language qualities of the dissertation

Formal and language qualities of the dissertation are above average.
Comment: Linguistically, the work is very good. Despite the author not being a native speaker, the text is written without grammatical errors, using correct, technical language.
The work is divided into four chapters and includes an introduction, conclusions, and a bibliography. Each chapter includes an introductory chapter on field emission theory and current knowledge on the effect of oxide layers on the properties of field emitters. In this chapter, the author also presents theoretical models of field emission and characterizes the basic research methods she will use in her work. The second chapter presents the aim of the work and a detailed list of sub-objectives. The third chapter presents the experimental methods employed by the author. Finally, the fourth and longest chapter discusses the results achieved by the author. This layout is sensible and well-organized, although it also introduces a certain difficulty in the form of the need to jump to chapter 3 when the results described in chapter 4 require a review of the production method. At times, it seems as if the text lacks all the information about the experiments conducted, but it is there, but you have to find it. Perhaps if the text included more frequent references to the chapters in which the descriptions of individual experiments are found, it would make reading and analysing the text easier (such references appeared several times, but not always).
There are minor errors in the work, which are normal in a work of this length, but in the future, it's worth trying to catch them before final submission, e.g.,
- the numbering of some formulas is missing, e.g., on pages 24 or 36.
- there are a some typos and misspellings, which I won't present here.
- at the Fig. 4.8, the legend below the charts is misleading, it is probably connected to Fig. 4.8b, but as it is below Fig. 4.8a, it may be interpreted as belonging to it, and there is another legend which is different.
- on page 69, author R_a value for oxide layer made in 10^3 Pa, but don't put the reference value for oxide made in 10^4 Pa, which may be somewhere in a table, but since she is comparing those values here, it should be put in.
- in chapter 4.7.1.3, author is describing Hydrofluoric Acid Cleaning, where she uses precleaning method in DI-ethanol mixture, but later in summary chapter 4.7.1.4, she refers to the mixture as DI-isopropyl alcohol, this is definitely a mistake because in the same paragraph she correctly states that "combination of water and ethanol was especially effective". But such mistakes shouldn't be present in a doctoral dissertation.
- in table 4.7 almost every value has its standard deviation, but the thickness of the 5 V anodized layer is mentioned as 1 – 23 nm.
These are the most serious editorial errors which I spotted, but they do not significantly detract from the reception of the work.

Ad f) The dissertation fulfils the conditions of Section 47 (4) of the Act

The dissertation fulfils the conditions of Section 47 (4)*) Act No. 111/1998 Sb. Higher Education Act: YES

((4) Studies are duly finished with a doctoral state exam and dissertation defence, which prove the ability and readiness to work independently in the field of research or development, or in theoretical and creative arts. The dissertation must comprise original and published results or results accepted for publication.*

Ad g) Creative abilities of the student in the given research field. Compliance with the standard requirements placed on the dissertations in the given field.

The doctoral student did prove his/her creative abilities in the given research field and the work does comply with the standard requirements placed on the dissertations in the given field.
Comment: In her thesis, the doctoral candidate demonstrates excellent skills in working with systems for material composition analysis, while also skilfully analysing the acquired data. She is comfortable working with technologies for producing tungsten oxide layers and tungsten field emitters. She efficiently performs electrical measurements of the obtained emitters and thoroughly analyses their usefulness. The entire work is well thought-out and organized. These attributes make mgr. Zuzana Košelová, worthy of being awarded a doctorate in microelectronics.

Overall evaluation: The presented work meets all the requirements for doctoral theses. The author begins with an in-depth analysis of the state of the art, both in terms of the fabrication and application of field emitters and the possibility of tuning their properties by depositing thin dielectric layers on their surfaces, particularly tungsten oxides. She presents the theory of field emission and its development over time and characterizes the analytical methods that can be used to analyse the fabricated layers and emitters. After this introduction, the aim of the work is presented along with the detailed goals the author aims to achieve, allowing for a clear conclusion. The author then describes how she performed the technological processes, measurements, and simulations. The main chapter, which comprises over half of the work, is devoted to the results and their analysis. In this chapter, the author truly demonstrates her analytical skills and the extensive work she performed during the technological development and analysis of the composition and parameters of the fabricated layers. A similar analysis and description of the technological developments is repeated during the fabrication and cleaning of field emitters. Ultimately, the author spends the least time analysing the properties of the emitters themselves. Nevertheless, this analysis is detailed and demonstrates the author's expected impact of various layers on emitter behaviour. The work concludes with a summary that demonstrates the achievement of the intended goals. The author of this review also confirms that the author's goals were achieved. Looking at the overall scope of the work, however, I wonder if the topic of the work is well-matched to the content. It is common knowledge that a doctoral thesis title is often defined at the beginning, only to discover later in the process that the scope of the planned work is excessive. This may have been the case here. The title of the work refers to layers deposited on emitters, and it is undeniable that the author also intended to utilise the deposition process. However, in her work, the layers made are produced by growth on the substrate via oxidation. In her work, the author correctly calls the process "layer growth" most of the time. Therefore, I would consider this an oversight. Despite this, looking at the evaluation comments stated above and on the achievements documented, i.e. author of 2 publications as a first author and co-author of 3 other publications in renowned Journals. Author and presenter of 6 conference contributions and co-author of 2 conference contributions. The conference presentations were very well received, as confirmed by numerous awards and honourable mentions, as

well as one contribution was invited lecture. The scientific contributions of mgr. Zuzana Košelová are starting to be cited by other researchers, which also shows that the work she has done is of great importance to others.
In summary, I, again, recommend awarding mgr. Zuzana Košelová her doctoral degree.

Opponent's questions:
I would like to ask:

1. Can you comment on the title of the work, concerning my comment above?
2. In Fig. 1.5 you are presenting "Examples of possible tip defects from our inspections", but all of those are just plain SEM images and in the chapter you are explaining that a lot of other analyses can be done using SEM, so why didn't you show some of those examples?
3. On page 40, Fig. 3.1 you show "difference between one and two step etching. For polycrystalline material needs to be used two-step method". In the text you are also stating that you will use two step etching method for fabrication of your emitters. May I ask why and what is the difference between one and two step etching?
4. In chapter 3.2 you are explaining surface cleaning procedures, which later on you are applying and discussing, especially in reference to cleaning the tungsten tips before oxidation, because it is important to clean the native oxide from the tips. But here you are writing that for tungsten sheets that you are firstly making the analyses, you are just using deionized water and ethanol. So what about the native oxide on the sheets? Could it change the properties of grown oxide layers on flat surfaces?
5. What is the cause of the high fluctuations in current value of thermally oxidized emitters (Fig. 4.27d)?
6. In the introduction you stated that the tungsten oxide is attractive candidate for reducing energy spread of electron emission. Did you try to check if your samples have low energy spread? If not, how would you measure the energy spread of emitted beam?
7. Your emitters have quite high turn on voltage. How can you lower this value in the future?

I ☒ **recommend** ☐ **do not recommend** **the dissertation for the defence.**

Date: 05.11.2025

Signature: ………[redacted]…………..