EVALUATION REPORT

on the thesis
for awarding the scientific degree "doctor of physical sciences"
in the professional field
4.1 Physical Sciences (Physics of Condensed Matter),
following the procedure for defense in the Faculty of Physics
of Sofia University "St. Kliment Ohridski"

The evaluation report was written by: **Assoc. Prof. Marushka Sendova-Vassileva PhD – Central Laboratory of Solar Energy and New Energy Sources – Bulgarian Academy of Sciences**, in her capacity of a member of the scientific jury According to Order № RD 38-464 / 27.07.2022 of the Rector of Sofia University.

Subject of the Thesis: "Surface Photovoltage Spectroscopy of Semiconductor Optoelectronic Materials and Nanostructures"

Author of the Thesis: Assoc. Prof. Vesselin Todorov Donchev, PhD

I. General description of the submitted documents

1. Information about the submitted documents

The candidate **Assoc. Prof. Vesselin Todorov Donchev, PhD** has submitted a thesis and a synopsis as well as the obligatory for the Faculty of Physics tables from the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions at Sofia University "St. Kliment Ohridski".

The documents submitted by the candidate for the competition comply with the requirements of ZRASRB, PPZRASRB and the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions at Sofia University "St. Kliment Ohridski "(PURPNSZADSU).

2. Details about the candidate

Vesselin Donchev graduated with honours from the Faculty of Physics at Sofia University "St. Kliment Ohridski" as a qualified physicist specializing in solid state physics. He defended a thesis on "Investigation of the electrical and optical properties of point defects in gallium arsenide" and obtained his PhD degree in Physics in April 1991. He started his scientific and teaching career as a staff physicist in the Department of Solid State Physics and Microelectronics of the Faculty of Physics at Sofia University in 1991. He has occupied the positions of senior and chief assistant and since 2004 he has been an associate professor in the Department of Condensed Matter Physics and Microelectronics. He has paid many visits for shorter or longer periods at a number of renowned foreign universities and research centres in France, Sweden, Switzerland, Brazil, Germany, Great Britain, where he has carried out specific scientific research, the results of part of which are used in his thesis for the scientific degree Doctor of Science. Assoc. Prof. Vesselin Donchev has extensive international experience in the organization and administration of scientific research as an Administrator of scientific projects under FP7 of the European Commission in the field of nanoelectronics and microsystems from 2010 to 2013. His teaching activities include a variety of general and specialized courses, supervision of a student laboratory, supervision of graduate students and one doctoral student who have successfully defended their theses. Currently he is supervising another PhD student.

3. General description of the candidate's scientific achievements

The thesis on "Surface Photovoltage Spectroscopy of Semiconductor Optoelectronic Materials and Nanostructures", presented by Associate Professor Vesselin Donchev, PhD for the acquisition of the scientific degree Doctor of Physical Sciences, is written in English on 172 pages, consists of an introduction, 4 chapters, a statement of scientific contributions, a list of publications included in the thesis, and a list of cited literature consisting of 300 titles. Each chapter or section of a chapter ends with conclusions that summarize the most important points of the exposition and help to make it clearer.

The first chapter is an overview and gives an idea of the current state of scientific research in three main areas, which are fundamental to the thesis, namely epitaxial semiconductor nanostructures, GaAs-based dilute nitrides and the technique and applications of surface photovoltage spectroscopy. All three subjects are concisely and informatively considered in enough detail for the reader to get their bearing in the following chapters and further reading is indicated in the cited literature in case of necessity and interest.

The second chapter is wholly dedicated to the surface photovoltage spectroscopy. The experimental equipment designed and constructed with the participation of the author is described. This is the equipment used for the experiments which are the subject of the thesis. Its advantages and specifics in comparison with other similar experimental set-ups are highlighted. Separate sections of the chapter are dedicated to some original approaches concerning the phase of the surface photovoltage, which have the character of scientific contributions, as well as to the vector model for representing the surface photovoltage signal, which facilitates and illustrates the analysis of the experimental results.

The third chapter is dedicated to original scientific results from the application of the method of surface photovoltage spectroscopy for investigation of various specific nanostructures suitable for particular optoelectronic applications. It consists of 4 sections, each of which is dedicated to a different type of nanostructure. In the first section are presented the results of surface photovoltage spectroscopy applied to AlAs/GaAs superlattices with embedded GaAs quantum wells. The second section is dedicated to interdiffused InAs/InGaAlAs quantum dashes-in-quantum well structures for light emitters. In the third section, structures with InAs quantum dots-in-quantum well for infrared photodetectors are considered. In the fourth section, multilayer structures with InP/GaAs type II quantum dots are investigated.

In all four sections, the main method of investigation is surface photovoltage spectroscopy, and in each of the cases it is applied for the first time, or practically for the first time, in such volume and depth to the specific type of nanostructures. The analysis is very precise and detailed, always using the spectrum of the surface photovoltage phase and in most cases applying the vector model to clarify and visualize the specific situation. In order to supplement and substantiate the explanation of the observed phenomena, other experimental methods such as photoluminescence, TEM, AFM, as well as model calculations are used.

Chapter Four is dedicated to investigations using surface photovoltage spectroscopy of materials and structures applied in solar cells. It consists of two sections. The first section comprises such investigations of silicon nanowires obtained by metal-assisted chemical etching. This material is promising for antireflective coating of silicon solar cells. Tests were made on samples of this material before and after chemical treatment of the surface to remove structural defects that appeared as a result of the etching process. Two different photon fluxes, high and low, and two different frequencies of modulation were used for the measurement of the spectra of surface photovoltage. The obtained spectra were analyzed in detail. The diffusion length of the minority carriers was determined. It is shown that the nanowires prepared by metal-assisted chemical etching have a high concentration of positively charged surface recombination centres, which reduce the lifetime and diffu-

sion length of charge carriers. The role of surface chemical treatment for the significant reduction of the number of surface defects and improvement of the applicability of the material for photovoltaic purposes has been confirmed.

The second part of the fourth chapter is devoted to GaAs-based dilute nitrides. The samples that were studied were obtained by the rarely used method of liquid phase epitaxy. It turns out that the surface photovoltage spectroscopy method is also rarely used to study dilute nitrides. Dilute nitrides of composition $In_yGa_{1-y}As_{1-x}N_x$ and $In_yGa_{1-y}As_{1-x-z}Sb_zN_x$ obtained by liquid-phase epitaxy, nearly lattice-matched with GaAs, were studied. The influence of the addition of nitrogen, indium and antimony on the width of the forbidden zone of the obtained alloy was established. For these studies, in addition to surface photovoltage spectroscopy, methods such as photoluminescence, EDX, SEM, X-ray structural analysis, Hall measurements and model calculations were used for additional information. A difference was found in the values obtained for the width of the forbidden zone in the studied samples by surface photovoltaic spectroscopy and by photoluminescence, the former being lower by 35 – 40 meV. A well founded explanation of this experimental result is given, related to the presence of a tail of defect states below the conduction band edge.

At the end of this chapter, solar cell structures based on GaAsSbN are presented. The structures were analyzed in detail by measuring surface photovoltage spectra, temperature dependence of photoluminescence with low and high excitation intensity, Hall effect. The mechanism of separation of the carriers in the photovoltaic structure was clarified. The current-voltage characteristics under standard conditions and the spectrum of quantum efficiency of the solar cells were measured. The results are comparable to those obtained for similar structures but fabricated by MOCVD.

The thesis concludes with a statement of original contributions and a list of publications included in it.

a) The publications included in the dissertation cover and in some cases significantly exceed the minimum national requirements and, accordingly, the additional requirements of the Faculty of Physics of SU "St. Kliment Ohridski" for obtaining the scientific degree "Doctor of Physical Sciences". Specifically, the minimum required points under indicator Γ of the national requirements are 100 points, while the candidate has 400 points, which is much more. The additional requirement of Group I publications included in the dissertation is 14, while the candidate has 15 such publications. In addition, in 9 of them, the candidate is required to have a substantial contribution. In this case, there are 14 such publications, which is significantly more. The additional requirement of independent citations in refereed publications is 100, while the provided Scopus reference for the candidate shows 382 such citations, and my

last check showed 387. This is in significant excess of the minimum criterion and the additional requirement of the Faculty of Physics. The additional requirement of an h-index of at least 6 (without self-citations) is also exceeded by the applicant who has an h-index of 9.

b) the scientific publications included in the thesis do not repeat those from previous procedures for acquiring a scientific title and academic position;

c) I am not aware of any legally proven plagiarism in the submitted thesis and synopsis.

4. Qualitative analysis of the applicant's scientific and applied scientific achievements contained in the materials for participation in the competition

The contributions presented correctly and in detail at the end of the thesis and the synopsis are of three main types. The construction of the experimental equipment for acquiring surface photovoltage spectra has the character of improving an existing method for measuring physical quantities and characterizing semiconductor samples. The definition for the first time of the zero value of the phase of the surface photovoltage and the proposed and applied new approaches for extracting information from the spectrum of this phase have the character of a new method, supplementing an already existing one, for the study of semiconductor samples. The studies of semiconductor superlattices with embedded quantum wells, multilayer structures containing quantum dots, series of dilute nitrides with different compositions obtained by liquid phase epitaxy, silicon quantum wires and solar cells based on dilute nitrides on the one hand demonstrate the potential of the proposed new and improved methods and approaches, and on the other hand represent the creation of new knowledge and knowledge complementing already existing data about the relevant semiconductor materials and structures. In particular, the investigation of dilute nitrides obtained by liquid phase epitaxy by the method of surface photovoltage spectroscopy is of a pioneering nature

The importance for the scientific community of the proposed advanced approach for measuring and analyzing spectra of the amplitude and phase of the surface photovoltage signal is confirmed by the high number of citations of the articles where these methods are presented and examples of their application are given, namely F2 – 108 times , F6 – 33 times, F13 – 13 times. In all of these publications Associate Professor Vesselin Donchev has a leading role, and of the last article, a tutorial, he is the single author. In publications presenting results obtained using surface photovoltage spectra in combination with other research methods, the selected semiconductor samples and structures are interesting and promising for modern applications such as semiconductor lasers, infrared photodetectors, optical memories, solar cells. This makes the obtained data useful for practical applications in optoelectronics and energy conversion.

5. Critical notes and recommendations

I have no critical notes.

6. Personal impressions of the candidate

I have known Vesselin Donchev since my student years. He has always impressed me as a serious and thorough researcher. We recently participated together in a European project under the COST program related to photovoltaics. There he was one of the most active participants, impressed others with his competence and managed to interest many colleagues from different countries and involve them in joint research. This resulted in joint publications, projects and continued collaboration after the end of the COST project.

7. Conclusion

After having familiarized myself with the presented thesis, synopsis and other materials, and based on the analysis of their significance and the scientific and applied scientific contributions contained in them, **I confirm** that the scientific achievements meet the requirements of the Law of Development of Academic Staff in the Republic of Bulgaria and the Regulations for its application and the relevant Regulations of SU "St. Kliment Ohridski" for obtaining the scientific degree "Doctor of Physical Sciences". In particular, the candidate satisfies the minimum national requirements in the professional field of **4.1 Physical Sciences (Physics of Condensed Matter)** and no plagiarism has been found in the thesis, synopsis and scientific works submitted for the competition.

I give my **positive** assessment of the thesis.

II. GENERAL CONCLUSION

Based on the above, I **recommend** that the scientific jury award **the scientific degree "Doctor of Physical Sciences"** in professional field **4.1 Physical Sciences (Physics of Condensed Matter)** to Assoc. prof. Veselin Todorov Donchev, Ph.D.

20.09.2022 Evaluation prepared by: .....

(Assoc. prof. Marushka Sendova-Vassileva, Ph.D.)