Opponent’s review of the doctoral thesis

entitled

Ultrafast photoconductivity and charge carrier transport in semiconductor nanostructures: a study by terahertz spectroscopy

by

Vladimir Pushkarev

The thesis submitted by Vladimir Pushkarev addresses the transport and confinement of electrons in semiconducting nanostructures and the impact of the distribution of their characteristics on global electronic properties. The transport is investigated by several contactless techniques mainly based on the time-domain terahertz (THz) spectroscopy and subsequently interpreted using microscopic models developed in the group and by the candidate himself. Considering the applied potential of nanostructured semiconductors, for example in the solar cell research and development, I consider the understanding gained in the thesis highly relevant for modern applications.

The thesis is structured into 5 chapters. The first introductory one gives an overview of various types of THz spectroscopic techniques and explains their methodology. The second chapter covers the THz response of nanostructured systems after an optical excitation: from the most common classical photoconductive models to semiclassical and quantum descriptions, the effective medium theory, and the “VBD” model developed in the candidate’s group. The chapter also includes the candidate’s original work: the calculation of the analytical solution of the wave equation for the effective sample response within the VBD model. The third chapter describes in detail the used spectroscopic setups and their performance.

The experimental results are presented in the following two chapters. First, networks of silicon nanostructures are studied in four THz spectroscopic setups, providing the access to rarely seen THz and mid-IR spectral bandwidth, ranging from 0.1 to 100 THz. The measured room- and low-temperature spectra are very carefully analyzed and compared with a large number of calculations and models. The investigation is presented in a highly coherent and methodological manner, and each experimental step, decision or partial interpretation is well argued and supported by models or qualified estimates. The candidate comes to the conclusion that the network of silicon nanocrystals has much wider distribution of sizes than inferred from electron microscopy analysis and proves that the THz spectroscopy provides an important complementary insight and could help to improve the synthesis.

The second part of the experimental work focused on lithographically prepared array of GaAs nanobars. Quantum mechanical calculations helped the candidate to explore the confinement of photoexcited electrons in a quantum potential. It was shown that band bending at the edges of the nanobars has a significant impact on the confinement and generates an electric field which triggers depopulation of regions close to the surfaces. This fact was experimentally confirmed by the near-field THz microscopy.

My overall impression of the thesis is very positive. It showed that the candidate is not only a skilled experimentalist but also ready to perform a modeling that requires a deep understanding of microscopic processes in the photocarrier transport. He also demonstrated his mastery of complex fitting with many free parameters and sophisticated data processing, for instance involving convolution and determination of an instrumental function. The thesis is written in perfect English with virtually no errors or typos, all graphs are of publication quality, and the presentation of the scientific ideas is very reader-friendly. In fact, whenever I had a question about an interpretation or an experimental suggestion, it was immediately addressed in a subsequent paragraph. In this respect, the reader's experience is very satisfying. My only critical observation is a few incorrect references to equations and typos in quantities, which are listed at the end of the review, and the 4-level numbering of section headings, which sometimes made the navigation more complicated.

Overall, I find the presented results to be original, very carefully analyzed, and relevant to the field. Due to the high level of the thesis, the candidate has demonstrated a good aptitude for his future independent scientific work. **Therefore, I recommend that this thesis is accepted and defended as a doctoral thesis.**

Possible questions for discussion:

1. The model of reflection and transmission in Fig. 8 and Eq. (2.10) is based on two relevant interfaces. However, the studied multilayered samples contain multiple interfaces that can be treated by the transfer-matrix approach. Can you estimate the impact, if any, of this consideration in the used model?

2. In Table 1, you state that the spectral resolution of the used THz setup is 0.1 THz. What defines or limits this resolution instrumentally? How could it be improved, if necessary?

3. For the fitting of the distribution of the nanostructure sizes [p. 50, Eq. (4.4)] and the D parameters [p. 81, Eq. (5.4)], two different distribution functions are used: the log-normal and the Gaussian, respectively. Can you comment on the particular choice of these distribution functions in these cases and not employing, for example, the inverse Gaussian function?

4. The distribution of the D parameters, which is related to the capacitance of the nanobars, is inferred from the fitting of data in Fig. 48. It shows a significant contribution of the cases where D = 0. What do you think is the physical meaning of such a case?

5. In Figs. 28 and 30, you compare the fitting by the original VBD model with later improvements by quantum-mechanical considerations. In my eyes, the new model sometimes does not necessarily match the data better; for example, the convex shape of the original model seems to fit better the real part of the low-temperature data for x = 0 and 0.3 or imaginary part in many cases. Can you comment on this comparison?

List of typos and mistakes:

- page 6, last paragraph: variables t and τ inconsistent with Fig. 3 and the preceding paragraph
- page 12, below Eq. (2.6): k should be squared
- page 12: references to Eq. (3.6) are inconsistent
- Eq. (2.20): n should be N_e as in Eq. (2.17)
- page 18: reference to the Drude model (3.2) seems inconsistent
- page 18: reference to Eq. (3.7) is inconsistent with (2.22)
- Eqs. (4.1): brackets should be all squared
- page 28: references to Eqs. (3.33) and (3.38) seem inconsistent

Prague, March 1, 2023

RNDr. Lukáš Nádvorník, Ph.D.
Department of Chemical Physics and Optics
Faculty of Mathematics and Physics
Charles University