Review Report on PhD Thesis

Faculty: **Central European Institute of Technology**
Brno University of Technology in Brno

Academic year: **2019/2020**

Student: **Ing. Michal Horák**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **prof. RNDr. Tomáš Šikola, CSc.**

Reviewer: **Ao. Univ.-Prof. Dr. Joachim R. Krenn**

PhD thesis title: **Electron microscopy and spectroscopy in plasmonics**

Topicality of doctoral thesis: The optical properties of nano- and microstructures are an important and highly active research area, for their relevance in both, fundamental and applied fields. On one hand, extreme regimes of spatial and temporal localization are addressed, where nanostructures show optical responses strikingly different from the well-known macroscale. On the other hand, these properties enable novel approaches to fields as solid state lighting, photovoltaics or sensing. Particularly strong effects are due to plasmon excitations in metal nanostructures. Plasmonic effects have been intensively investigated in recent years, ranging from tailored optical near fields, spectrally selective scattering and absorption and ultrafast dynamics to strong coupling to quantum emitters single molecule sensitivity in sensing.

It is within this field that Ing. Michal Horák choses his research topic, and he does so in a certainly highly actual manner by addressing the spatial and spectral field profiles in lithographically tailored nanostructures. In particular, with transmission electron microscope (TEM) based spectroscopies (electron energy loss spectroscopy, EELS and cathodoluminescence (CL)) he applies state-of-the-art methods that are have been introduced to this field only recently. It is thus evident that this Thesis addresses current research field in a timely manner. Its results are original and provide significant novel scientific insight.

Meeting the goals set: It should be pointed out right away that results from this Thesis have been already published in four articles in high impact journals, including two recent papers with Ing. Michal Horák as the first author in *Scientific Reports* (2018) and (2019). A surprisingly long list of further publications on topics related to, but not directly associated with this Thesis as well as more than 20 conference participations illustrate that Ing. Michal Horák is very effective in his scientific work. I can confirm that he has certainly met the goals set for this Thesis, which include to apply TEM-EELS/CL to plasmonic

nanostructures, including the development of sample preparation, to explore complementary plasmonic geometries with a view on Babinet's principle, to probe specific plasmonic nanostructures for their electric and magnetic hotspots and to investigate silver amalgam as a novel plasmonic material.

Problem solving and dissertation results: The author presents a clearly organized and written Thesis of about 130 pages. Following an introduction and an outline of the Thesis structure, he introduced the reader first to „Analytical electron microscopy". This chapter gives an excellent overview on electron-matter interactions, with discussions on the fundamentals and the basic technological aspects. In the following chapter, „Electron beam spectroscopy in the field of plasmonics", Ing. Michal Horák first introduces the physics of plasmons, leading over to the aspects of probing electrons. I can certainly recommend these parts as standard reading for entering the field.

The following part, „Fabrication and characterization of plasmonic nanostructures" is on one hand discussing the basics of sample fabrication by chemical synthesis, ion beam lithography and electron beam lithography. On the other hand, it includes a study on the EELS and CL signals from different structures, including the effect of the substrates and the comparison with numerical simulations. On this basis, the chapter on „Plasmonic antennas fabricated by electron beam and focused ion beam lithographies" (based on *Scientific Reports* (2018)) presents a comparative study on circular gold nanodisks fabricated with either method. It is clearly demonstrated that electron-based fabrication features sharper edges, a more homogeneous height profile and less contamination and it is thus to be preferred for most applications. In „Babinet's principle for disc-shaped plasmonic antennas", said principle is tested for circular nanodisks and holes (based on *Scientific Reports* (2019)). Extensive spectrally and spatially resolved data confirm the qualitativy validity of Babinet's principle. Importantly, the limits of the quantitative validity are clearly worked out, which gives as well an interesting view on the material and geomtery aspects of plasmonic structures in general. Babinet's principle plays as well an important role in the section on „Plasmonic antennas with magnetic and electric hot spots". Considering the role of electric and magnetic fields in Babinet's theorem, this part presents a detailed study on bow tie and diabolo particles and their aperture counterparts. Only to mention the most central points, the EELS and CL data clearly identify the plasmonic modes and their spectral geometry dependencies, as well as the formation of local spots of high field intensities that could be further exploited in various applications. Finally, in „Silver amalgam nanoparticles", this material is successfully investigated for its plasmonic properties, that are certainly of interest with a view on its relevance in electrochemistry.

The Thesis is completed with a conclusion, an extensive literature reference and a brief technical appendix.

Importance for practice or development of the discipline: As outlined above and as underlined by the publication of results achieved in the frame of this Thesis, the presented work is original and of high scientific significance. It is thus certainly enriching the discipline, providing numerous aspects for further research or application developments.

Formal adjustment of the thesis and language level: As outlined above, this Thesis is clearly organized and very well written, meeting thus all formal requirements. This includes the publication of Thesis results in high impact scientific journals.

Questions and comments: n/a

Conclusion: In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining a PhD degree. This Thesis is ready to be defended orally, in front of the respective committee.

Graz, November 29, 2019

Ao. Univ.-Prof. Dr. Joachim R. Krenn

CEITEC – Středoevropský technologický institut
Vysoké učení technické v Brně
Purkyňova 123, 612 00 Brno, Česká republika
www.ceitec.cz