

Ph.D. Thesis Review Report

Thesis by: Ing. Martin Hruška

Title: Utilisation of nanostructured and nanoporous materials for chemical sensors

Reviewer: Jan Grym, Ph.D., Institute of Photonics and Electronics of the CAS

This thesis represents a well-rounded study of black metal layers prepared by thermal evaporation with the aim of applying the layers in quartz crystal microbalance (QCM) and chemiresistive gas sensors. The thesis has been built up upon a hypothesis that nanostructured black metal layers with a high specific surface area provide more bonding sites for gas analytes than the corresponding solid layers, which should be reflected in the improved sensor sensitivity. It comprises three key tasks with logically developed hypotheses. The first task was to take advantage of the large surface area of evaporated black metals to increase the sensitivity of the QCM sensors. The second task was to exploit the increased resistivity of nanostructured black metals in the chemiresistors. The third task was related to the first one and was aimed at elucidating the viscoelastic properties of black metals during their formation by in situ impedance measurements and their analysis. Each task was addressed in one paper, of which the first two have been published and the third one is under review. Martin Hruška is the first author of all three papers and has also contributed to other papers related to the topic of the thesis.

In the first task, the black gold layers were shown to significantly increase the sensitivity of the QCM sensors towards water and EtOH vapors. Nevertheless, the use of thick black metal layers resulted in damping of the QCM oscillations. The origin of the damping was thoroughly investigated in the third task, where several hypotheses were developed. Impedance spectra were collected in situ during the deposition process, which provided insight into the growth of the black metal layer and the changes in its viscoelastic properties and acoustic impedance. It was observed that damping was not present when the black-metal QCM sensors were operated in vacuum, and that it strongly depended on the surrounding atmosphere of inert gases. This led to the conclusion that inert gases are not adsorbed but rather trapped within the porous black metal layer, which modifies the acoustic impedance and consequently causes a damping effect. Moreover, an extended Butterworth-Van Dyke (BVD) model was developed for layers exposed to atmospheric conditions. This approach introduces a new concept for QCM sensors based on changes in the viscoelastic properties of black metal layers. In the second task, the black gold layers employed as sensitive layers in the chemiresistors were shown to be capable of detecting hydrogen.

Conclusions related to these tasks are of great value to the scientific community dealing with chemical gas sensors and provide new insights, particularly into the field of QCM sensors with active layers formed by black metals. This thesis also significantly contributes to the understanding of black metal layer formation by thermal evaporation and its optical properties before and after thermal treatment.

The freely available software was developed by the author of this thesis. The BVD fitting software is available as a MATLAB toolbox for in situ analysis of QCM impedance measurements while the SensorDataAnalyst software was developed using the NI LabVIEW environment for an in-depth analysis of the sensor data by fitting the data with a first-order step response model.

The thesis is extensive, contains a large number of relevant references, addresses several research fields, and discusses physical and chemical phenomena, as well as technical solutions in deposition techniques and the development of software. It is written in good English, has a logical structure, and is easy to follow. There is a small number of clumsy expressions and typographic errors. Each subsection ends with brief conclusions that significantly help the reader follow key ideas. The author has clearly shown that he reviewed a large portion of the scientific literature and is well versed in a broad range of research fields.

I have the following questions and comments for discussion during defence:

- Briefly summarize the advantages and disadvantages of thermally evaporated black metal layers for QCM sensors in comparison with other deposition methods.
- Comment on the reproducibility of the preparation of black metals by thermal evaporation and also on the reproducibility and stability of the sensor characteristics.
- “The analysis shows a higher equivalent diameter obtained from AFM images, due to the technique's focus on surface morphology through van der Waals interactions. Conversely, the SEM, with its deeper penetration due to the high voltage of 30 kV, reports a lower diameter, especially for the nanoclusters.” (page 72) Does different acceleration voltage result in the observation of a different diameter of nanoparticles? Why?
- “In contrast to conventional annealing, these experiments were carried out under high vacuum conditions, which influence the thermal behavior through radiative heat dissipation. This environment suggests that the actual 'melting' temperatures required for specific morphological transformations may be higher than those observed in standard annealing procedures...” (page 74). Please develop this idea and clarify the meaning and context.

In my opinion, the results of this thesis are above and beyond the requirements for a doctoral degree. I am convinced that Martin Hruška is capable of independent scientific work, and I recommend that this thesis be defended.

Prague, August 8, 2024



Jan Grym, Ph.D.