

Review of Doctoral thesis by Nirmal Kumar

Title: Tungsten Oxide-Based Gas Sensors prepared by Advanced Reactive Magnetron Sputtering Technique

University: University of West bohemia, Pilsen

Supervisor: Doc. Ing. Pavel Baroch, PhD.

Consultant: RNDr. Stanislav Haviar, PhD.

The thesis deals with preparation, characterization and testing of thin films based on tungsten oxide for application in hydrogen gas sensors. The importance of the topic relates to the growing role of hydrogen as a green source of energy.

The work has been carried out in a systematic way, with suitable methods, the aims are clearly stated.

The results of the thesis bring new knowledge concerning the composition of sensing thin layers for hydrogen and improvement of preparation and testing techniques. The results were reported in four peer-reviewed papers, which confirm their originality.

The structure of the thesis is clear; it consists of three main parts. In the introduction a brief overview of gas sensors principles and so far used materials is given. It is rather encyclopaedic set of facts missing sufficient consistency. In the methodology part the principles of preparation and characterization methods are described. The main part consists of five original papers (one under review) with a brief introductory overview connecting the papers.

The thesis brings a lot of innovative results. I would appreciate mainly the use of the high-power impulse magnetron sputtering technique, which enabled preparation of sensing films with various stoichiometry and structure and highly improved their sensing properties. Also, the idea of Pd deposition on top of a sensing layer to reduce humidity interference is a high importance.

There are a few formal mistakes, such as repeating sentences (page 2, par. 1.2 at the beginning; page 3, par. 1.3 below the middle), edit remarks (page 18, at the bottom; page 21, at the bottom) and typos, nevertheless the thesis reads well.

The list of publications is missing, but papers, which are part of the theses, confirm good publication output.

Except for the publication C and D; it is not clear what the author's contribution was, but I assume it is on a similar level.

Questions and comments:

1. Is it possible to compare the sensing parameters of the studied layers presented in this thesis with results published in literature (based on tungsten oxide) or with commercial hydrogen sensors?
2. In the publication C, which is under review, there is rather speculative interpretation of the composition and morphology of the deposited Pd adlayers. It is a pity, that the author didn't use some surface sensitive technique, especially photoelectron spectroscopy, which could bring information about the chemical state of Pd. The conclusions are based on the results obtained on thick Pd layer, which could significantly differ from the small deposited amount. The small amount of Pd, which was used in the tested sensing layers, could be either highly dispersive (as the substrate has grain morphology with a large surface area) or amorphous. Also, the interaction of Pd with the substrate cannot be excluded. In the interpretation of sensing properties, I miss the possibility of a Pd catalytic effect. Please, could you comment on this?

Overall, the work is very solid and in my opinion Mr. Nimrat Kumar has fulfilled all the necessary requirements for granting a PhD. Degree according to the applicable laws. I would therefore recommend that the work should be accepted for the defence.

Praha 28.11.2021

Kateřina Veltruská

I find the main merit of the work in presenting the new system for sensing measurements and in the successful synthesis of materials with stabilised sensing response under a wide humidity range and at relatively low temperatures.

In conclusion, the submitted thesis fulfilling all the requirements for doctoral theses in the field and the author has shown his ability to independently work in the field of science. Therefore, I **do recommend** the submitted thesis for defence.

I do have several questions about the thesis:

1. Can the author elaborate on his tasks and results in papers A and D? Especially the HiPIMS model is a little bit different from the rest of the results focussed on the coatings themselves.
2. The student introduces several ways how to enhance sensing properties. One of them is to prepare porous films. This should be relatively easy to explore in magnetron sputtering by pressure changes. Could the author elaborate on this option?
3. How were the sputter yields in the HiPIMS models calculated? Could you please elaborate?
4. The tungsten target during the tungsten oxide depositions was DC powered. Were there no arcing problems?

In Brno, December 5, 2021



doc. Mgr. Pavel Souček, Ph.D.

Assessment of the doctoral thesis by Nirmal Kumar

**Tungsten Oxide-Based Hydrogen Gas Sensors Prepared by
Advanced Reactive Magnetron Sputtering Technique**

The submitted doctoral thesis reports on the research of new materials for thin film-based hydrogen gas sensors and the investigation of hydrogen gas sensing properties of such materials. The thesis first introduces a gas sensitivity measuring system developed by the author. Then it shows several different ways to enhance gas sensing thin films, including control of their crystalline structure, stoichiometry, their decoration by noble metal nanostructures and their multilayering. After these studies, two more gas sensor challenges are tackled – lowering the sensor's operating temperature and their independence of the humidity of the analysed gas admixture. The problem investigated in the thesis is very up-to-date and important in the field as is dictated by the shift from dirty to clean energy production. Hydrogen fuel cells are probably the most promising new technology to fulfil this goal. Unfortunately, working with hydrogen is difficult due to its wide explosive mix range, lack of visibility, smell or taste and even hydrogen flame is clear and nearly invisible. Therefore, hydrogen sensors are crucial for the future.

The thesis is a commented compendium of the author's papers (five in total – four published and one submitted). It is written in English and covers 89 numbered pages and 10 front-matter pages. It is divided into 6 sections. The first section Introduction succinctly describes the background in the workings of gas sensors and presents the current challenges and strategies to overcome them. The chapter also contains more than 100 references documenting the author's wide insight into the topic. Chapter 2 Methodology describes the deposition process and introduces the used analytical techniques. It also focuses on the developed system for the sensing properties. Chapter 3 Research objectives clearly states the objectives of the thesis. Chapter four Results consists of the individual author's papers— one paper per objective. Chapter 5 Conclusions comments on fulfilling the objectives, and chapter 6 summarizes the author's conference contributions.

The thesis is easy to follow and has an excellent graphical level. The structure is very clear. The thesis does contain some typos and errors, such as repeated sentences near the beginning of subsection 1.2 or a missing reference in subsection 2.1 to name the most obvious. However, these minor flaws do not undermine the overall very good level of the thesis itself.

The methods used to meet the proposed objectives are well chosen. The results are clear, and all the objectives of the thesis were successfully met. The results are internationally recognised, as can be seen by publishing them in impacted and respected journals.

The author presents five publications. Two were published in the International Journal of Hydrogen Energy, one in Journal of Physics D: Applied Physics, one in Materials and one for submission to Nanomaterials. The author also gave 5 oral and 4 poster presentations at different conferences. These show the high scientific quality of the author.