Review of the Ph.D. thesis titled „Resistive switching with chalcogenide thin layer"

Author: Mgr. Bo Zhang

Development of new types of memories is at these days an important research field and resistive switching memories are promising in future to replace present disc or flash-disc memories.

The submitted PhD thesis of Mgr. Bo Zhang deals with fabrication of resistive switching devices exploiting ionic Ag-doped chalcogenide thin film as electrolyte. Author tested five different memory geometries: (i) spot geometry, (ii) needle contact geometry, (iii) tip contact geometry, (iv) crossbar geometry and (v) via-hole geometry. In these memories either AsS_2 or $GeSe_2$ were applied as electrolyte and Ag was doped in the electrolyte layer by photodoping and dissolution from the top or bottom of electrolyte layer.

The thesis is well structured and has suitable format and sufficient length that is expected for a PhD thesis. All the studies presented in submitted thesis are well constructed and the conclusions are well supported by a lot of experimental work. The amount and quality of experimental results indicates a very good experimental proficiency and ability of systematic research work. Mgr. Bo Zhang shows a deep knowledge of the background of the field and good work with relevant literature. When I should reproach author for something then it would be quality of some Figures. Some are very illustrative (e.g. Fig. 27 or on page 74 Graphic illustration of sample preparation), some which contain an experimental data are too small (e.g. Fig 32d, Fig. 49 3D topological maps). On opposite side I would like to point out that text is clear, results are trustful and valuable and this thesis are significant contribution for development of fully functional devices exploiting resistive switching phenomenon.

I have following questions to applicant:

Question 1 According to data given in Experimental part, thin chalcogenide AsS_2 and $GeSe_2$ films were deposited by classical vacuum evaporation methods. It is well known that mainly in the case of Ge-Se based glasses composition of deposited thin films can significantly differ from composition of starting glassy ingot. Structure (and thus properties including ability of Ag photodissolution) can be significantly affected by conditions during their evaporation. Again, in the case of Ge-Se glasses structure depends significantly on angle of deposition (columnar structure) and eventual rotation of substrates. Did the applicant check real composition of prepared films and did he make some SEM studies of deposited $GeSe_2$ or Ag doped $GeSe_2$ films? I did not find such data...

Question 2 Applicant used altogether five different geometries of chalcogenide electrolytes. Is there any special reason why Ag doped $GeSe_2$ electrolyte was used only in the case of crossbar and via-hole geometry and vice versa Ag doped AsS_2 electrolyte only in remaining three geometries?

Question 3 I did not find in Conclusion answer on following question. Which of these five applied geometries applicant see as most perspective to be used in future for fabrication of resistive switching devices and why?

At the end I would like to state that the work "Resistive switching with chalcogenide thin layer" clearly meets criteria for a PhD thesis and I can recommend it with pleasure for the defence.

v Pardubicích 12. 8. 2017

prof. Ing. Miroslav Vlček, CSc.

External critique opinion for student **Mgr. Bo Zhang** of his PhD thesis:

"Resistive switching with chalcogenide thin film"

This thesis is about the research and development of new materials and devices suitable for future memory elements based on the resistive switching technology. The main aim of this work is to observe and characterize the formation of metallic silver filaments in the prepared chalcogenide layers and discuss the switching process. Such topic is very much up to date, because of the steeply increasing demand for new highly effective memory devices designed to have high capacity at low energy consumption.

In the theoretical part, the author discussed the principle of the resistive switching technology which is perspective for the construction of new highly effective memory devices. Even though they are able to function at low voltage and current conditions, they can exhibit fast response and long-term stable data storage with very low energy requirements. He gave the useful overview of the materials and their properties that are currently available for the construction of the memory devices, emphasising mainly chalcogenide glasses suitable for solid electrolytes. In addition, for the characterization of the switching process, he explained the measurement of current-voltage characteristics using the cycling voltammetry technique. Moreover, he discussed the mechanisms of diffusion, the methods of deposition, the geometry of a memory cell and its electrodes, the methods for the characterization of the cell, and cell parameters important for the application in memory devices.

In the experimental part, the author successfully fabricated resistive switching devices based on Ag doped chalcogenide thin films from the As-S and Ge-Se glass-forming systems that behaved as a solid electrolyte of sufficiently high ionic conductivity. The AsS_2 and GeS_2 electrolytes were doped with Ag by photo doping and dissolution from the surface layers of the electrolyte. For the prepared memory devices, fixed and floated types of electrodes in five different geometries were correctly tested, sufficiently characterized and discussed in detail; comprising spot, crossbar, needle contact, tip of conductive AFM, and via-hole electrode geometries. Each cell of particular geometry was characterized and its switching behaviour as well as other important properties were discussed, mainly from the point of view of their advantages and drawbacks for the intended application in the memory device. For this purpose the author correctly used SEM and conductive AFM methods. The obtained results indicate that the memory device based on cells with the via-hole geometry is the most promising solution for future commercialization.

The measured data are clearly presented in tables and figures of high quality, thus, the results give detailed insight into this research and contribute to the desired explanation of the possible mechanism of the resistive switching process. As the complete switching mechanism is still not completely understood, the results and conclusions gained from this research work are important and useful very much to support the filament model that currently represents the mostly accepted explanation. Hence, the achieved results are very promising for the further development and optimization of these memory devices.

The thesis is well-written, with only few clerical errors, and the style and layout is good. The achieved research outcomes are fully comparable with the results of other international research teams in this field.

Mgr. Bo Zang in his work clearly demonstrates creative and experimental abilities in this research field and the thesis meets the required standard of a doctoral thesis to justify the award of a PhD title. Therefore, I recommend the PhD thesis of Mgr. Bo Zang to be defended in front of the Board of Examiners.

Questions to be discussed:

1. Is it possible that the formation of the Ag metallic filaments can cause the generation of internal stress in the electrolyte layer? Could this affect the mechanical properties of the cell and its long-term stability under the condition of frequent cycling?
2. What causes the observed branching of the filaments? Is it possible to control or suppress this phenomenon?
3. Could you approximately estimate what is the ratio of ionic to electronic conductivity in your electrolytes?
4. How sensitive is the resistive switching process to temperature changes in case of your thin chalcogenide layer?

14th July 2017

Martin Míka

External Examiner/Opponent: Associated Professor Martin Míka

Department of Glass and Ceramics

University of Chemistry and Technology Prague

PhD Dissertation Evaluation

Resistive switching with chalcogenide thin layer

Author of the Dissertation: Bo Zhang

Resistive switching (RS) phenomenon has been known since 1960's and since then, the hysteretic RS behaviour under the applied electric field has been reported in many materials. Rapidly increasing publication output on the subject during the last decade indicates an attractivity of the phenomenon especially in the field of possible production of new generation a high-density, high-speed, and low-power non-volatile memories in semiconductor industry, i.e. in the production of resistive random access memories (RRAMs).

In the presented dissertation, RS-devices of five different geometries has been prepared and characterized. Studied RS-devices were based upon "simple" MIM' structure, where M, M' stand for suitable types of conductive (metallic) electrodes (an inert electrode – W, Al and/or Pt in this work, and an active one - Ag) and I denotes an insulator and/or resistive material (chalcogenide glasses – AsS_2 and/or $GeSe_2$ in the dissertation) which were "sandwiched" between the electrodes acting as solid electrolyte layer in which, under application of suitable bias voltage conductive Ag filaments were formed and/or dissolved. Switching between two different resistive states was the basis of functioning of the studied devices. Author's attention was especially turned to the characterization of the basic parameters of a switching behaviour of the prepared RS-devices to recognize advantages and drawbacks of the studied geometries as for their prospects in future potential commercialization. The important part of the work was dedicated to understanding of the conductive filament formation/dissolution by its direct observation with various microscopic methods. Thin films of the used electrolytes (AsS_2, $GeSe_2$) had, essentially, to be "preformed" before RS-behaviour experiments by photo-doping and photo-dissolution of part of Ag electrodes inside electrolyte materials. In some cases, also an influence of buffer layers inserted between some of the electrodes and electrolyte layer was investigated as well to evaluate its influence on the switching process and to eliminate extra losses of active electrode materials.

The dissertation itself is divided into an introduction, four main chapters, a conclusion and references part. The reference part contains 77 references and in the last part of the dissertation a list of author's publications and conference contributions. As for the references the opponent of the dissertation would expect more thorough literature search to reflect very latest results related to the dissertation subject (only seven references from 77 was published after 2014). Three author's articles published in impacted scientific journals and six conference contributions can be considered as an averaged dissemination of the dissertation results.

Very brief introduction part lacks more precise and more specific description of the rationale of the dissertation and its research goals. On the other hand, author in the next chapter quite exhaustively describes principles of the studied phenomenon, i.e. resistive switching, and its mechanisms, he presents a comprehensive list of the solid electrolyte materials exhibiting the resistive switching including the studied chalcogenides. He also describes in this chapter more perspective geometries of the memory cells based on the phenomenon as well as the basic parameters of the RS-devices investigated for their evaluation of their utilization in future potential applications. Also, he briefly reviews the ways of direct observation of the formation and/or dissolution of the conductive filaments.

The third chapter is dedicated to the description of experimental conditions used during the preparation of the studied RS-devices of five different geometries, their "compositions" as for the types of used electrodes and electrolytes and the conditions used during the "preformation" of the cells (or more precisely solid electrolytes) by photo-doping and photo-diffusion steps. I would recommend to the author insert here also the chapter 8 where author very clearly in graphical form presents individual steps used during the preparation of the cells of various geometries. The same is valid also for chapter 4 which could be inserted into this chapter as well.

The core of the dissertation is covered in the chapter 5 where on 25 pages the main results are presented and discussed. Authors here separately describes experimental results obtained for each of the prepared RS-devices with five various geometries. He presents here and discusses basic switching characteristics of the devices (I-V curves), for crossbar geometry he evaluates an influence of the buffer layer position and its functioning as for the switching behaviour of the devices. Significant part of the author's interests is dedicated to the observation of the formation Ag-filaments during the switching process and the proposal of possible explanation of its formation. Also, other aspects connected with the studied process are presented and discussed.

The final part called "Conclusions of thesis" can be more than conclusions considered as a brief review of work done during the study and only conclusion is, in opinion of the opponent, the preselection of via-hole geometry as a most perspective method for future possible applications based on the studied components, i.e. chalcogenide electrolytes doped with Ag from the active electrodes.

It has to be pointed out that behind the brief description of the work lies a large amount of experimental work connected with the preparation of the devices, their characterization and evaluation. Besides the above-mentioned objections, I would like to give the following comments and recommendations, and put a following questions to the author:

1. Apart from minor typing errors and stylistic mistakes in English text of the work which make some sentences meaningless, e.g. second one on page 17, I would recommend in future e.g. to give the reference for the book (?) [55] with direct Internet link as under given name is not possible to find it (probably is written only in Chinese language(?)).
2. Can the author comment on the potential advantages and/or drawbacks of RS-devices based on studied chalcogenides electrolytes against the broadly studied oxide systems?
3. What was the reason to study two different electrolyte system, i.e. Ag-doped AsS_2 and/or $GeSe_2$, and not consistently only one of them for all studied geometries of RS-cells? Can You comment on this?

As follows from the presented dissertation and as mentioned above, Bo Zhang proved his competence in scientific and research work. He contributed to the identification of future aiming of the research of RS-devices based on Ag-doped chalcogenide electrolytes. Despite the above mentioned critical remarks his thesis fulfilled all requirements and **I recommend this thesis to be defended.**

V Pardubicích 12.7.2017

Ing. Jiří Navrátil, CSc.