Doctoral thesis, the opponent review

Student: Ing. Tomáš Halenkovič Supervisor: Prof. Petr Němec

Co-supervisor: Assoc. Prof. Virginie Nazabal

Title: Chalcogenide thin films

Opponent: Assoc. Prof. Zdeňka Kolská (Materials centre of Ústí nad Labem, Faculty of

Science, J. E. Purkyně University in Ústí nad Labem)

The presented dissertation thesis is based on a cooperation of two institutions (Faculty of Chemical Technology at University of Pardubice and Institut des Sciences Chimiques de Rennes) collaborating for a long time in the field of development of new materials for optics and optoelectronics.

This thesis is focused on study of amorphous thin films of ternary Ge-Sb-Se and Ga-Sb-Se systems fabricated by co-sputtering technique for their potential applications in the field of nonlinear optics. General quality by means of morphology and topography, linear and non-linear optical properties and local structure of created films depending on the composition were discussed. The aspect of co-sputtered thin films was also studied. Moreover, the optical properties and structure of quaternary Ge-Sb-Se-Te thin films prepared by RF sputtering as a potential alternative to ternary systems were studied.

The thesis is divided into several parts, the Theoretical one, Experimental part, Results and Discussion and Conclusions. Experimental part describes the own samples preparation and subsequent characterization by many methods (density determination, DSC, SEM, EDS, XRD, Ellipsometry, AFM and Raman spectroscopy). The used methods are suitable for these kinds of materials and sufficient for this kind of research.

The aims of this thesis were (i) to prepare selenium based amorphous thin films from ternary Ge-Sb-Se and Ga-Sb-Se systems using RF magnetron co-sputtering technique; (ii) determination and study of optical properties by variable spectroscopy methods; and (iii) study of optical properties and structure of quaternary Ge-Sb-Se-Te thin films prepared by RF sputtering.

The presented dissertation thesis contains many new valuable results in the relevant research area.

The theoretical part is very clear, comprehensive and it is based on many literature sources. All work is clearly written almost without typing errors, I have almost no question.

Division of all work is very "friendly" to readers. It is very sympathetic the placement of literature sources from which the student drew, always behind the given chapter. This is very clear and easy to find all of information. Also the Concluding remarks placed at the end of all subdivision in part of Discussion and Conclusions are very pleasant.

Finally, I evaluate very positively the comparison of the obtained data with literature sources when available and possible.

I have the following questions or remarks to student:

1) On p. 58 student describes the density determination of the sample by determining mass in air and in the reference fluid. In my opinion this determination is not well described. However the sample weight is the same in the air or in some liquid. In my opinion, therefore, it is rather the volume of the sample using the reference fluid and the subsequent determination of

density. The sentence of: "The solid is first weighed in air (m_A) and then again (m_B) in reference liquid (e.g. ethanol)" and also the relation 3-1 is not correct in my opinion.

- 2) Fig. 2-4 (SEM micrographs) is very unclear and the changes are very slight at a given resolution. In this case, it would be better to use the better resolution. To same comment I have for Fig. 2-12, at which the resolution is even "the worse" (at Fig. 2-4 the resolution of 100 nm, but at Fig. 2-12 even only $2 \mu m$). Why the resolution was not be used the better or, at least, the same for all samples.
- 3) The deposition parameters for thin films preparation are presented in Tab. 2-4. Why so many variables are here (power of Ga₂Se₃, power of Sb₂Se₃ and deposition time)? Why, some of them, e.g. the deposition time was not the same for the same power values? Or have been these parameters tested and optimized previously and set up for the creation the layers of required composition?
- 4) On the other hand I do not understand the deposition parameters in Tab. 2-6. How at the same power and Ar pressure the obtained values of thicknesses and compositions are different? (e.g. the samples no. 1 x 5 or 2 x 6, etc). In my opinion something is missing in description of these parameters.

Despite the minor comments, the presented dissertation thesis brings new knowledge and many new, interesting and valuable results in the field of study and development of new materials for optoelectronics. This is also evident from the publication activity of the student. Therefore, I strongly recommend this thesis to the defense.

Ústí nad Labem, 14. 1. 2019

Assoc. Prof. Zdeňka Kolská