

Report on the PhD Thesis „ Chalcogenide thin films“ by Tomáš Halenkovič.

The thesis considered is devoted to the current issues namely to the materials convenient for application in the non-linear optics and to the materials prospective as a phase change materials (PCM). The choice of amorphous chalcogenides is good choice because these materials have high non-linear refractive index, some of the amorphous chalcogenides show reversible phase change transition, some of the amorphous chalcogenides are photo-sensitive ones, respectively. Choice of the concrete materials is perfect. Ge-Sb-Se glasses are well transparent even to 11  $\mu\text{m}$ , have high refractive index, are more stable than sulphur based glasses, do not contain dangerous elements like arsenic and their properties can be tailored by the chemical composition modification and/or by the way of the material preparation. Ga-Sb-Se and Ge-Sb-Se-Te thin films represent new materials which seem to be promising as PCM and materials convenient for incorporation of rare earth elements (Ga-Sb-Se).

The thesis is written and organized in a modest and classical way. The main output of the thesis is condensed in the chapter 2 and namely in the chapter 3. The author realized considerable amount of the experimental work especially in the field of thin films preparation and in an extensive characterization of the films prepared. The broad spectrum of characterization methods was used and the data evaluation and discussion reflects up-to date knowledge of the problem considered. The main contribution of this work, in my opinion, can be summarized as follows: (i) The finding of the conditions of the thin films preparation by RF magnetron co-sputtering. Certainly huge work was done and I express my compliment. (ii) The preparation of amorphous thin films of Ga-Sb-Se glasses along the  $\text{Ga}_2\text{Se}_3 - \text{Sb}_2\text{Se}_3$  line even up to  $\text{Ga}_2\text{Se}_3$  amorphous thin film. (iii) Preparation of amorphous Ge-Sb-Se-Te thin films. (iv) The determination of the basic optical parameters like linear and non-linear refractive index, optical band gap and response of the as-prepared thin films on the illumination by near band gap photons.

I have only few remarks to the thesis considered.

(i) For a reader it is pity that an illustration of quite good optical quality of as-prepared thin films, see the paper by Halenkovic T., et al., J. Am. Ceram. Soc. 101 (2018) 2877-2887, is not presented in the thesis.

(ii) Some values of the Urbach edge slope, see Table 2-3 are really quite high. One reason for that ones, as pointed out by the author, could be the high structural disorder of the as-prepared (virgin) samples. However could it be that the ellipsometry and the model used is not ideal for the study of

absorption in the Urbach edge region in thin films? For instance if one considers the fact that the density of states responsible for Urbach absorption is two orders of magnitude lower than the density of states responsible for the "band gap" absorption we measure too weak absorption relevant to Urbach tail using the sample with the thickness of order 800 nm. Hence, the error in determination of the Urbach edge slope could be quite high. I suppose that at least measurements on the well relaxed (annealed) samples and probably comparative measurements on the bulk samples can help in understanding of the rather high values of the Urbach edge slope determined.

(iii) In the connection with photo-sensitivity of the samples studied, see Table 5-1, let me to mention that very often the illumination of virgin thin films leads simultaneously to irreversible and reversible photo-induced changes. Hence, for better understanding of photo-induced changes it is appropriate to study the photo-induced response on both virgin and well relaxed (annealed) samples. For more accurate estimation of the magnitude, and the sign, of photo-induced band gap ( $dE_g$ ) it would be better to examine the photo-induced band gap shift in relation to the number of absorbed photons rather than to the photon flux only.

(iv) There are some printing errors in the thesis considered, for instance p. 17 ( $E_U = \gamma$  in Eq. (1-2), [20]), evidently should be  $E_U = 1/\gamma$ , p. 40 Ge-Ge + Se-Se  $\rightarrow$  Ge-Se should be Ge-Ge + Se-Se  $\rightarrow$  2 Ge-Se etc.

The remarks above are not a critique of the work considered. The printing errors exist everywhere and they are not an essential measure of the thesis quality. Moreover I am bad searcher of errors. The thesis summarizes the interesting and new results of the huge amount of the experimental work in preparation of the materials and their characterization. I am sure that the results of this thesis will be very useful for forthcoming research in the relevant field and probably also for some application. The author showed good ability for orientation in the problem, for experimental work and also for evaluation, discussion and presentation of the results he obtained. I recommend accepting this work for the defense and for further proceedings for an appointment of the candidate for a degree: Doctor of Philosophy.

  
Ladislav Tichý