Photoinduced changes in amorphous gallium doped GeTe₄ chalcogenides

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Abstract. Chalcogenide thin films from the system Ge-Te-Ga were deposited by thermal vacuum evaporation on glass substrates from initial bulk synthesized materials. Optical measurements on as-deposited and irradiated thin films were performed. The optical constants - refractive index (n) and extinction coefficient (k) were evaluated from the transmission and reflectance spectra. Irradiation of the films for 3 hours through an interference filter with pass-band centered at 1,06 µm led to changes in the transmission spectra of the samples. A shift of the absorption edge was observed depending on the gallium content. The most significant change in the absorption edge was obtained in films with composition (GeTe₄)⁹⁵Ga⁵ with estimated coordination number 2.43. According to the covalent network model in glasses with coordination number close to 2.43, a floppy-rigid transition occurs. The spectral distribution of the refractive index change showed a sign inversion – from negative to positive. Changes in the physical thickness of the samples investigated due to the irradiation were not established.

1. Introduction
Chalcogenide glasses are based on the chalcogens – S, Se or Te. These glasses are low-phonon-energy materials and are generally transparent from the visible to the infrared regions. Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photoinduced effects as a result of exposure. These include photo-crystallization or amorphization, photo-polymerization, decomposition, contraction or expansion, dissolution of metals and light-induced changes in local atomic configuration. These changes are accompanied by changes in the optical constants, i.e., changes in the electronic band gap, refractive index and absorption coefficient. These effects are favored in chalcogenide glasses due to their structural flexibility and also due to their high-lying lone-pair p states in the valence bands [1].

Chalcogenide glasses only exhibit photo-induced changes in the physical thickness (volume changes like photoexpansion or photocontraction), photodarkening (red shift in the band gap) and
photo-induced changes in the phase state. These phenomena do not occur in crystalline chalcogenides, or in any other amorphous semiconductors [2]. Consequently, it is very important to describe and understand the interaction of chalcogenides with light. There are also application reasons: the photoinduced effects in glasses can be used for production of photoresists, optical memories, diffraction elements, optical light-guides, optoelectronic elements and devices [3, 4, 5].

2. Experimental
Thin films of the GeTe$_4$ system with additives of gallium up to 20 at.% were deposited by thermal evaporation in vacuum onto glass substrates.

The experiments were performed in a Leybold LB 370 vacuum installation at residual gas pressure of 1.33×10$^{-4}$ Pa. The film deposition conditions applied were: source-substrate distance 0.12 m, temperature of evaporation source 800−900 K, measured by a Ni-NiCr thermocouple.

The thin films’ structure was investigated by X-ray diffraction and the composition was proved by Auger electron spectroscopy within the accuracy of the method, namely, ±1 %.

Transmission and reflection spectra of the thin films before and after irradiation were measured using a double beam UV/VIS/NIR computer controlled spectrophotometer (model Cary 5E Australia) in the spectral range 400÷2500 nm at room temperature.

The irradiation procedure was performed using a halogen gas lamp at maximal power density 60 mW/cm$^2$. The lamp-sample distance was chosen to be 0.25 m and the duration of the light illumination was three hours for each sample through an interference filter with pass-band centered at 1.06 µm.

3. Results and discussion
The amorphous state of the thin films deposited was proven by X-ray diffraction. The chemical composition of the films was found to be close to the composition of the targets used. The shift of the optical absorption edge was determined from the transmission spectra (figure 1). The dependence of the absorption edge shift on the gallium content in glasses at transmission T=10% is presented in figure 2.

![Figure 1. Transmission spectra of (GeTe$_4$)$_{1-x}$Ga$_x$ (x=5, 10, 15 and 20 at. %) thin films before and after irradiation.](image-url)
The further addition of gallium leads to a change of the sign of the shift - from photobleaching (blue shift) to photodarkening (red shift) effect. The transition in the glasses starts at 10 at. % Ga, where an absorption edge shift practically does not occur. The most significant shift in the absorption edge is observed in the film with 5 at. % gallium. These effects could be explained in the framework of the covalent network model [6, 7, 8]. According to this model, a floppy-rigid transition is to be expected in glasses with coordination number close to 2.4. In our case, namely, a film with composition $\text{(GeTe}_4\text{)}_{95}\text{Ga}_5$ the calculated coordination number is 2.43 and such a transition is most likely to take place. A further gallium content increase in the films reduces the effect of the absorption edge shift and changes the sign of the effect towards photodarkening.

The basic optical constants—refractive index ($n$) and extinction coefficient ($k$) were evaluated from the transmission and reflection spectra using the Levenberg-Marquardt procedure [9]. The change of refractive index $\Delta n$, as the difference in the $n$ values after exposure ($n_{\text{exp}}$) and before exposure ($n_v$) is calculated using the refractive index spectral distribution profile for as-deposited and for irradiated thin films. Figure 3 shows the spectral distribution of $\Delta n$ for all samples investigated.

It is very important to note that the sign of the refractive index change is in good correlation with the absorption edge shift dependence on the gallium content, presented on figure 2. The constant value of $\Delta n$ at 10 % Ga in the films in the entire spectral region supports our assumption for a structural transition in the glasses studied. The sign of the refractive index change, positive or negative, is the
same as the one observed in the absorption edge shift, $\Delta \lambda$. The compositional dependence of $\Delta n$ at the wavelength 1500 nm where these materials are of practical importance is presented on figure 4.

\[ \Delta n = n_{\text{exp}} - n_{v} \]

at $\lambda = 1500$ nm

Figure 4. Compositional dependence of $\Delta n$ at 1500 nm.

Thus, the addition of gallium up to 20 at.% in the films converts the negative change of the refractive index into a positive one. In addition to the presented photoinduced changes of $\Delta \lambda$ and $\Delta n$, no evidence of photoexpansion or photocontraction was observed. Irradiation, therefore, leads to changes in the optical thickness $(nd)$, while the physical thickness $(d)$ remains constant.

4. Conclusion
Irradiation of the thin films causes a shift of the absorption edge depending on the composition. The spectral distribution of the refractive index change also depends on gallium content in the films. The sign of the $\Delta n$ was found to change from negative to positive. No variation was observed in the physical thickness of the samples investigated after irradiation. The behavior of the absorption edge and refractive index modulation could be explained with re-organization of the atomic structure due to a floppy – rigid transition. Addition of a third element – Ga up to 20 at.% changes the optical response of this system.

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