



Photo- and ion-induced changes in amorphous chalcogenide films

PhD thesis

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Introduction

Amorphous chalcogenides together with elemental chalcogens, beside of the amorphous silicon and germanium, constitute one of the most important groups of the solid inorganic semiconductor materials. Depending on the composition, their physical properties vary in a wide range. They have an important property to undergo various specific, peculiar only to chalcogenides, structural transformations under the action of external influences (temperature, light, electric field, high-energy ionizing irradiation).

These structural transformations are accompanied by the change of their electric and optical properties. Therefore, they have found several applications in information technology and optoelectronics. Thus, the physics of these phenomena is important not only for the fundamental science, but it has also practical significance. The technological progress and the continually growing miniaturization raise new and new demands towards the materials to be used, requires deeper knowledge of the properties of these materials and thin films and nanostructures made of them.

Aims

There are lot of publications in the literature devoted to the structural transformations and optical changes observed in chalcogenide glasses and amorphous thin films irradiated with various high-energy particles and light particularly. At the same time, only a few papers dealing with the effect of ions have been published.

Therefore, we aimed to investigate the effect of medium energy H^+ and D^+ ions on the structure and optical properties of amorphous Se, AsSe and As_2S_3 films and to compare it with light-induced effects.

Furthermore, we planned to investigate a recently discovered phenomenon - the interdiffusion induced by visible light in some amorphous chalcogenide multilayers and the optical changes and volume expansion connected to it, particularly:

- to develop multilayers of new composition and improve properties of the known ones by deeper unraveling of the photo-induced processes taking place in them and by perfection of the preparation technology of multilayers;
- to carry out high pressure and photoluminescence measurements and to elaborate a theoretical model for the photo-induced interdiffusion;
- to investigate the effect of irradiation by light ions on the structure and optical properties of the multilayers.

Results

- I. I have investigated and compared the effect of H^+ and D^+ ions of 40-180 keV energy and light of $\hbar\omega \geq E_g$ photon energy on the structure and optical properties of amorphous Se, AsSe and As_2S_3 films prepared by thermal evaporation by means of visible-infrared transmission spectroscopy, selected wavelength transmission, Raman scattering and x-ray diffraction measurements.
 1. I have shown that the effect of ion irradiation on the optical properties of the films, namely on transmittance, absorption edge and refractive index dispersion, is qualitatively similar to the well known effect of light. Ions as well as light cause increase of the refractive index and darkening. i.e. the shift of the optical absorption edge towards lower energies. Depending on the thermal history of the film, these changes are partly or entirely reversible [1,2].
 2. By means of the Wemple-DiDomenico-analysis of the refractive index dispersion and Raman scattering measurements we have experimentally proven that the changes in short and medium range order caused by ion irradiation in As_2S_3 are identical to the known photo-induced ones [2].
 3. By means of x-ray diffraction and optical measurements I have shown that in selenium films ion irradiation – similarly to light – has a crystal growth rate enhancing effect, too [3].
- II. I have studied some problems regarding the mechanism of the light and ion irradiation induced interdiffusion and related optical absorption edge blueshift and volume change in amorphous chalcogenide multilayers prepared by thermal evaporation, the terms of taking place of these phenomena and their relationship with the structure and optical properties of the component materials.
 1. We have developed two new photosensitive multilayers (Te/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$) – possessing higher and faster optical changes than earlier ones – which due to the photo-induced interdiffusion related transmittance, refractive index and volume changes can be applied for amplitude-phase optical recording [4,5,11].
 2. We have shown that the application of high hydrostatic pressure decreases the rate of photo-induced interdiffusion in Se/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ multilayers. With the help of a new method we developed – by measuring the pressure dependence of the optical bleaching accompanying the interdiffusion – we have determined the activation volumes of the photo-induced interdiffusion. From their relatively high values (0.48 and 0.41 average atomic volumes for the Se/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ respectively) we have concluded that the photo-induced interdiffusion in these multilayers very likely happens by means of creation and motion of vacancy-type point defects [6].

3. We have shown that the photo-induced interdiffusion leads to the increase of the photoluminescence intensity in Se/As₂S₃ multilayers. The detailed analysis of the spectra has led us to the conclusion that in its beginning stage the photo-induced interdiffusion is more intensive in the selenium layers. At the same time neither the selenium layer thickness nor the interdiffusion had any effect on the photoluminescence peak energies. This can be connected with the peculiar properties of the luminescence centers, high localization of the charge carriers that lead to the absence of quantum size effect in luminescence [7,8].
4. I have developed a thermal spike model for the photo-induced interdiffusion. For low light intensities it reflects qualitatively correctly the experimental behaviour of the macroscopic parameters of photo-induced interdiffusion, e.g. the temperature dependence of the coefficient of interdiffusion and gives a quantitatively good estimation of the interdiffusion coefficient in Se/As₂S₃. It also was successful in explaining the asymmetry characteristic to the initial stage of the interdiffusion experienced in the photoluminescence experiments. According to the model it is because within a bilayer the light absorption is strongly inhomogeneous – almost all light is absorbed in the layers having narrower band gap, while in the layer with wider band gap almost no or at least much less light is absorbed. With the proceeding of the diffusion the absorption inhomogeneity decreases [9].
5. Basing on experimental studies I have ascertained that the interdiffusion, caused by irradiation with 180 keV D⁺ ions in Se/As₂S₃ and As_{0.2}Se_{0.8}/As_{0.2}S_{0.8} multilayers among the models of ion beam mixing can be described best by the thermal spike model. Comparing the data with the results of our studies of photo-induced diffusion, bleaching and volume change, I have shown that the light- and ion irradiation induced interdiffusion and the related optical and volume change are similar in many aspects. This, particularly the similarity of the temperature dependence of the kinetics of bleaching related to the intermixing, supports the basic assertion of the above mentioned model that the photo-induced diffusion can be described as a thermal spike phenomenon [10].

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