Holographic investigations of photoinduced changes in PECVD Ge-Se thin films*

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The photoinduced changes in thin films of the Ge-Se system, where the ratio of Ge:Se ≈ 1:2, prepared by PECVD technology, are investigated by holographic methods.

The temporal dependence of diffraction efficiency at constant intensity of a laser beam is investigated for scalar and polarization recording. A typical initial maximum is observed, attributed to a change in transmission. The recording has amplitude-phase character.

The maximal value of the diffraction efficiency in both cases is approximately 10^-2%. The calculations show that the photoinduced change in the refractive index |n_i - n_0| ≈ 2.10^-3. In order to induce photoanisotropy, longer exposure is needed and |n_i - n_0| ≈ 2.10^-3. The electron microscopic analysis of the irradiated (exposure E ≈ 250 J/cm²) and non-irradiated sample does not give information of a substantial change in the film topology.

The results obtained are compared to those of films prepared by vacuum-thermal evaporation. They show that there is no substantial difference in the value of photoinduced changes. That indicates that the medium order of the films that is associated with the method of their synthesis is not of considerable importance for the promotion of photoinduced changes. The results are interpreted in view of the theory of soft configurations and defects in disordered systems. Copyright © 1996 Elsevier Science Ltd

Introduction

The photoinduced changes in chalcogenide glasses possess features that attract the researchers’ interest. They are associated with the lone-pair electrons and low coordination number of the chalcogenide atoms that are the reason for strong electron-phonon coupling and cause great mobility of a number of local atomic configurations. These phenomena have been investigated in many aspects and, among the different chalcogenide glasses, the greatest attention has been given to the germanium chalcogenides. The main object of these investigations have been thin films of the foregoing, prepared usually by vacuum evaporation. One of us has previously reported results on the preparation of thin films of the systems As-S and Ge-Se by plasma enhanced chemical vapour deposition and the great advantage of producing films with exact stoichiometry in a wide range of combinations of the two elements.

The present work reports on holographic investigations of the photoinduced phenomena in thin films prepared by PECVD. The interest of the holographic technique as a tool for elucidating the mechanism of photoinduced changes, has increased due to its high sensitivity and unique ability to follow the course of the photoinduced changes by measuring in real time the diffracted light from induced gratings. Owing to its high sensitivity, the holographic method is especially suitable for analysis of low sensitivity materials and thin films.

Experimental

The investigated films were deposited on glass substrates in a plasma discharge stainless steel reactor. The precursor gases were high purity hydrides, H₂Se and GeH₄, pure or diluted in hydrogen (15 mol % of the hydrides). A low pressure plasma, varying between 0.1 to 1 mbar, was excited by an RF discharge (13.56 MHz) between two parallel plate electrodes, 8 cm in diameter as described in Ref. 6.

The composition of the films were determined by an electron microprobe analyzer was close to the ratio Ge-Se ≈ 1:2 and film thickness was about 1 μm.

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A standard interferometric configuration with a spatial frequency of 200 mm⁻¹ was used and the diffraction efficiency measured in real time with a 1.7 mW He-Ne laser at λ = 632.8 nm. The arrangement permitted both scalar and polarization holographic recording as described in Ref. 7. The thin films were investigated before and after illumination by scanning electron microscopy.

Results

Figure 1 shows the change in transmission with time at λ = 488 nm and intensity of an Ar⁺ laser I = 2.5 W/cm². Initially, a strong increase in transmission is observed after which it nearly restores its original value in about 2.5 s. Further illumination of the sample brings about an insignificant increase in transmission. Similar behavior was observed by Song et al. The oscillations at the beginning of the illumination are not fully understood. We suppose that a non-radiative recombination occurs in the chalcogenide glasses that is released via self-trapped excitons that return to ground state after excitation (maybe thermal) caused by the illumination, i.e. these effects are due mainly to pho-

Figure 1. Change in transmission with time at λ = 488 nm and intensity I = 2.5 W/cm² for the sample with composition Ge\textsubscript{51},Se\textsubscript{49.5}.

Figure 2. SEM photographs of (a) illuminated (exposure E = 250 J/cm²) and (b) non-illuminated sample with composition Ge\textsubscript{51},Se\textsubscript{49.5}.

Figure 3. Temporal behavior of the diffraction efficiency in scalar recording for the sample with composition Ge\textsubscript{51},Se\textsubscript{49.5}.

Figure 4 shows the diffraction efficiency dependence on time in polarization recording. It is evident from the curves that in order to induce photoanisotropy (birefringence), longer exposure is needed and |n₁ - n₂| ≈ 2.10⁻³. According to Fritzsche, the light-induced optical anisotropy in chalcogenide thin films is produced by non-radiative geminate recombination events that occur in the absorbing microvolumes and cause local changes in atomic bond configurations. It may be suggested that polarized light not only creates new defects, but orients the existing intrinsic defects mainly in one direction along a particular optical axis.
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Adding the complexes to the chalcogenide glasses may enhance these effects as we have found for thin films of Ge$\text{As}_{71}S_{29}$, in which the maximum value of the photoinduced birefringence is $\Delta n = 0.016$, i.e. eight times greater than that of the samples that we measured in the present investigation. That is probably related to the appearance of Weigert-effect in these films.

The diffraction efficiency behaviour after cessation of the illumination is shown in Figure 5. Relaxation processes, typical of glassy materials are observed.

It may be shown that the dark relaxation of the photoinduced changes is described by the fractional-exponential law of Kohlrausch $\exp(\frac{-t}{\tau})^\gamma$ where $0 < \gamma < 1$ and $\tau$ is relaxation time, depending on the value of the photoinduced changes. Such a relaxation dynamic is attributed to the structural elements, i.e. in the beginning the smallest structural elements relax. It may be assumed that these are selenium chains with limited length, enabling the relaxation of increasingly bigger elements, which are tetrahedral units of selenium with germanium atoms. The hierarchical limitation of the photoinduced anisotropy dynamic explains its slower decrease with time, as shown in Figure 5.

With these investigations we practically observed all kinds of photoinduced phenomena, both in films of pure Se, and in Ge-Se films of various compositions, including those identical to films investigated and produced by vacuum evaporation. The results for the scalar recording show that the values of the photoinduced changes or films prepared by PECVD, have the same order of magnitude as films produced by vacuum evaporation. Bearing in mind that the method of film preparation affects mainly the medium order, it may be concluded that it is not of considerable importance for the photoinduced processes in chalcogenide glasses. This is further proof for the applicability of the suggested mechanisms, treating the phenomena within the chemical bond, by which the open structure of chalcogenides permits low coordination atoms and coordination defects to swing and flip into adjacent void regions to form new band configurations.

Similar results are obtained on comparison of the vacuum evaporated As$_2$S$_3$ and AsS, as well as spin-coated As$_2$S$_3$ and AsS thin films.

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**References**