Thickness homogeneity of $Ge_xSb_{40-x}S_{60}$ chalcogenide thin films

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The thickness homogeneity of thin chalcogenide $Ge_xSb_{40-x}S_{60}$ films evaporated on glass substrates is investigated. The problem has been tackled by studying the transmission having in mind that inhomogeneities in thin films have a large influence on the optical transmission spectrum. The effects of thickness variation and surface roughness on the transmission spectrum have been considered. It has been found that the film thickness is rather homogeneous over the film area. The inconsistency of the experimental and theoretical oscillations in the transmission spectra indicated inhomogeneities due to surface roughness. An atomic force microscopy study has shown a roughness below 50 nm over an area of 10x10 μm. Second harmonic generation scanning has also revealed rather good homogeneity over the film area.

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1. Introduction

Chalcogenide glasses based on sulfide, selenide and telluride alloys in binary or multi-component systems exhibit excellent transmission in the near and far infrared spectral regions [1]. They are high refractive index materials with a nonlinear refractive index typically 100 times that of silica, and the with a low maximum phonon energy [2]. The high chemical and thermal stability allows the creation of easy-to-prepare optical devices. Furthermore, chalcogenide glasses are very important materials owing to their photosensitivity, as this allows the preparation of writing channel waveguides [3].

A very important advantage of using chalcogenide glasses in integrated optics is their availability as thin films. As a result, it is important to know the layer thickness homogeneity with high accuracy and precision at the nanoscale. As with all optical devices it is also important to characterize the linear optical constants accurately, so that their non-linear optical properties can be identified.

The aim of the present paper is to investigate the thickness homogeneity of thin chalcogenide films of the $Ge_xSb_{40-x}S_{60}$ system evaporated on glass substrates. The effects of thickness variation and surface roughness on the transmission spectrum have been considered. The problem has been tackled by studying the transmission having in mind that inhomogeneities in thin films have a large influence on the optical transmission spectrum. In this study the approach suggested by Swanepoel [4] has been applied for a thin absorbing film on a transparent substrate. The inhomogeneities due to surface roughness have been studied by atomic force microscopy (AFM) and second harmonic generation (SHG) scanning over the film area.

2. Experimental details

Thin films from the $Ge_xSb_{40-x}S_{60}$ system (x varying between 10 and 35) series were deposited on glass substrates by thermal vacuum evaporation of powdered parent glasses synthesized from the elements with 5N purity. The deposition rate was ~ 80 - 100 Å/s. The film thickness was controlled in situ by MIKIFFV quartz sensor devices.

The compositions of the deposited films were found to be very close to that of the parent glass, as checked by microprobe analysis.

The linear optical transmission spectra in the visible range have been measured using a Specord-M40 spectrophotometer at two slit widths of 2.5 and 5 mm.

The thicknesses of the films were measured using a MII-4 (LOMO) interference microscope.

The SHG was studied in transmission geometry. A YAG:Nd^{3+} laser beam (λ_1=1064 nm, pulse duration 30 ns and pulse energy 1 mJ) was directed onto a sample as a pump source for SHG light with λ_2=532 nm. The SH signal was detected by a photomultiplier and fed into a computer-controlled data acquisition system. SHG from a platelet of x-cut α-SiO_2 crystal at the Maker fringe maximum was used for calibration of the setup. The SH intensity from the $Ge_xSb_{40-x}S_{60}$ films was measured as a function of the angle of incidence θ by rotating the sample around an axis lying in the film plane.

A P4-SPM-MDT atomic force microscope was used to characterize the surface roughness of the chalcogenide films.

3. Results and discussion

The absorption and the nonlinear SHG optical characteristics of the $Ge_xSb_{40-x}S_{60}$ films examined in the present study depend substantially on the film composition (x). The relation of x to the bonding structure of the films, represented by the average co-ordination number of the covalent bonds Z, can be resented as Z= [4x+3(40-x)+2*60]/100, where 4, 3 and 2 stand for the co-ordination numbers of Ge, Sb and S, respectively [5]. The co-ordination number Z is a useful parameter in further considerations since it characterizes the structure of the atomic units [6].

The small-scale homogeneity of the films was characterized by transmission measurements and AFM images.

The results of the transmission measurements for the investigated films with different x values are shown in Fig.1.

Most of the films exhibited similar transmission curves with pronounced interference fringes in the visible range below the fundamental absorption edge. The clearly seen interference fringes indicate a uniform film thickness.

The only exception was the film with x=27, where a smooth transmission curve was observed. As found earlier [4], thickness nonuniformity or a graded change over the film area would have a destructive effect on the interference phenomena, and consequently result in a smooth transmission curve.

The measurements at the two slit widths would allow a better estimation of possible thickness inhomogeneity [7]. In the case of a significant linear variation in the film thickness on a macroscopic scale a decrease of the slit width would cause expansion of the interface pattern [7].

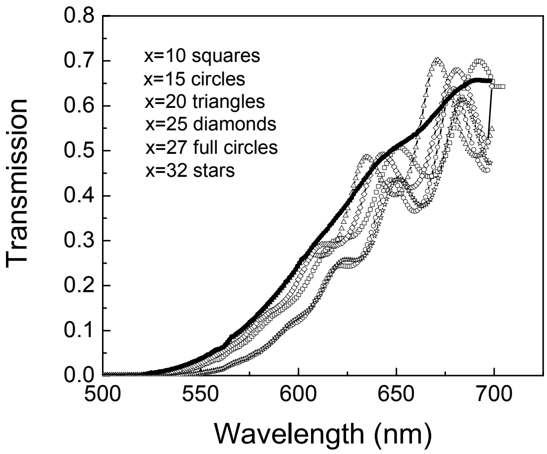

Fig.1. Experimental transmission spectra for films with different compositions x.

The results revealed that this variation in the thickness is relatively small for all investigated films. This is evident from Fig.2, where transmission curves taken at two different slit widths are presented. Confirmation is drawn from the fact that both curves follow a similar track, with very close positions of the extrema.

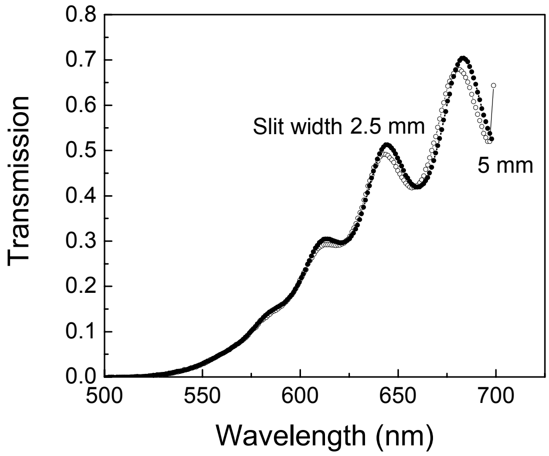

Fig. 2. Transmission spectra measured at two slit widths for a film with composition $Ge_{25}Sb_{15}S_{60}$.

If the film thickness is supposed to be uniform, the theoretical transmission spectra can be fitted to the experimental one. The results from the film transmission measurements, together with the calculated transmission curve for a film $Ge_{35}Sb_5S_{60}$ film are plotted in Fig. 3. It can be seen that the amplitude of the oscillations in the calculated curve is higher that in the experimental curve. This can be regarded as an indication of surface roughness of the films [7], which could also contribute to smoothing of the transmission curve.

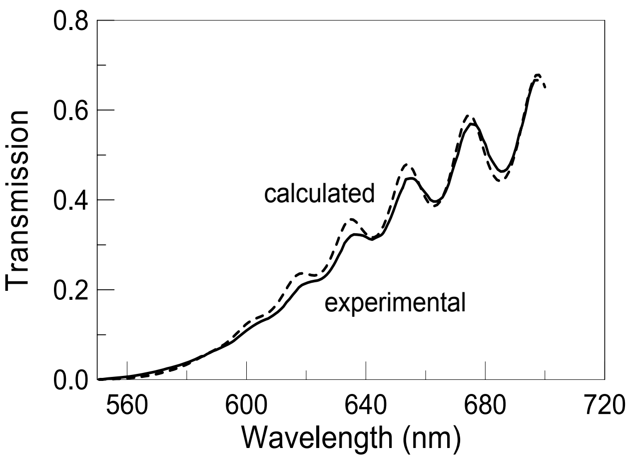

Fig. 3. Experimental and calculated transmission curves of the $Ge_{35}Sb_5S_{60}$ film.

For all investigated films the surface roughness, as assessed by AFM scans, was not more than 50 nm over an area of 10x10 μm, compared to the whole thickness of about 1300 nm. This is of the same order as found by other authors [8]. As evident from the 3D image in Fig. 4, even for the film with x=27 with the smooth transmission spectrum, the surface roughness is of the order of 30 nm.

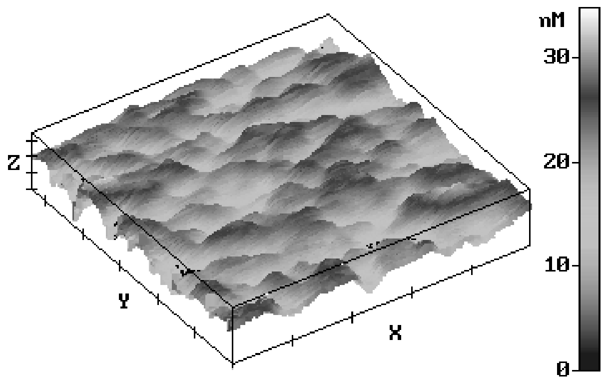

Fig. 4. 3D AFM image of the $Ge_{27}Sb_{13}S_{60}$ chalcogenide film over an area of 10x10 μm.

From the results presented above it can be inferred that the investigated thin chalcogenide films reveal good homogeneity even on the nano-scale.

For application purposes, however, it is important to characterize the film homogeneity on a large scale.
In order to check the thickness variation over the whole film surface, measurements of the thickness at two edges of the film (Position 1 and Position 2), as shown in Fig. 5 (top view of the structure), have also been performed. The results are presented in Table 1. Even though the differences in the thickness amounted for some of the films (x=25) to up 110 nm, it should be remembered that this variation is over the whole film area of 1.5 cm^2. Still, the linear thickness variation over the light spot area in the transmission measurements is comparable to the roughness magnitude. This fact characterizes the used film deposition method as optimized, when systematic thickness variations do not exceed the statistical ones.

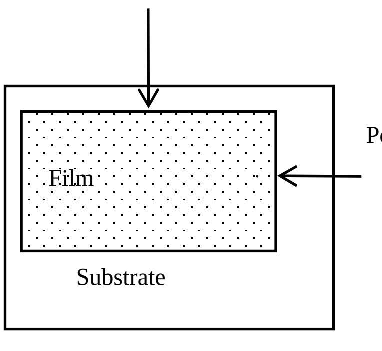

Fig. 5. Positions for the measurements of the thickness of the films.

Table 1. Thickness of films with different compositions x.

Film composition, x	Thickness at position 1, nm	Thickness at position 2, nm
10	1450	1410
20	1460	1470
25	1540	1430
27	1300	1290
35	2840	2930

Another possibility forr addressing the problem of the homogeneity of the films over a large area is offered by measurements of the nonlinear optical response. SHG scans have already been used to investigate the homogeneity of different materials.

It should be remembered that the SHG is a very sensitive technique in respect of film inhomogeneity. A SHG scan over the film surface is shown in Fig. 5. It can be seen that the signal variations do not exceed the measurement accuracy of 15 %. These variations are again over the whole film surface as for the step measurements, and consequently can be considered as showing good homogeneity not only of the thickness, but of the entire film.

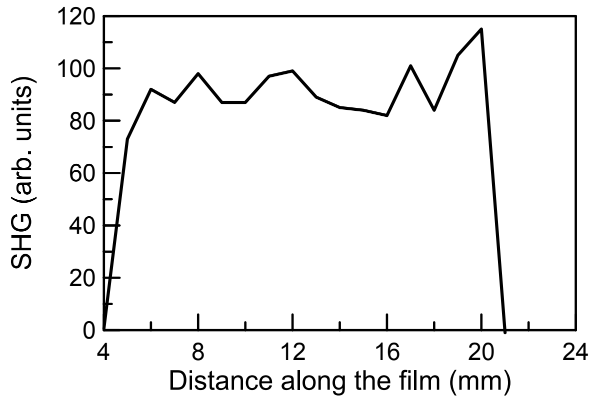

Fig. 5. SHG signal scanned over the film surface along the film edge.

One point that still needs clarification is the smooth transmission spectrum of the film with x=27. This is the film with a coordination number Z=2.67. It has been suggested that at this particular composition a transition in the film structure is observed, from a 2D layered structure to a typical glassy 3D spatially cross-linked network [9]. Moreover, this compoisition belongs to the so called "stress-rigid" phases with an average coordination number of $2.6<Z<2.8$, where significant photo-induced structural transformations are observed. A similar 2D-3D phase-transition has often been reported for non-stoichiometric chalcogenide glasses [10]. It can be suggested that the nonuniformity in this case is related to nano-scale composition inhomogeneity rather than to thickness variations. A previous XPS study has shown that rearrangement of the structural units causes a change in the short range atomic order [11]. Measurements of different properties of the chalcogenide thin films have confirmed the onset of a structural transition at x=27 [12].

4. Conclusions

The results presented in this work have shown that the thin films of the $Ge_xSb_{40-x}S_{60}$ system are rather homogeneous even on the nano-scale, as revealed by a detailed study of the transmission characteristics and AFM images. The film homogeneity was also proved by step edge measurements and SHG scans over the whole film area, which is important for large-scale applications.

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