AMORPHOUS CHALCOGENIDE NANO-MULTILAYERS: RESEARCH AND DEVELOPMENT

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Abstract

Investigations of photophysical processes in amorphous chalcogenide semiconductor layers were extended during the last decade towards the nanostructures. Nano-layered films or nano-multilayers (NML) were in the focus of the development of new photosensitive, optical recording media. A short review of the progress made in the technology of new NML structures and in the understanding correlations between stimulated interdiffusion and optical transformations, surface relief recording is presented. This is the text of the abstract.

I. Introduction

Chalcogenide glasses are versatile semiconductor and dielectric functional materials. Besides the basic photoconductivity and good IR optical transparency, they possess a number of well known and widely investigated peculiar properties like photo-induced change of optical parameters, electrical switching, optical non-linearity. These were reviewed in Refs. [1]-[4] and have been applied in devices: electrophotography, X-ray photoreceptors [5], Ovonic switch [6], holographic gratings [7], waveguide sensors [8],
all optical switch [9], RW CD [10] and others. In spite of a wide range of compositions in binary, ternary and more complex systems of chalcogenide glasses [11] the problem of smooth or abrupt modification of parameters still exists. These modifications can be performed partially by the special technologies (cooling rate, special thin film deposition) or by creating complex artificial structures as known in microelectronic technology. Following the example of microelectronics which turned to the nanoelectronics on the way to the smaller and more efficient devices exploiting new properties of the crystalline semiconductors at nano-scale, scientists drew attention on amorphous materials. The first were amorphous hydrogenated silicon and similar amorphous semiconductors which served the basis for creation of amorphous superlattices, which are usually defined as nano-multilayers [12, 13]. Multilayer structures are the simplest artificial nano-structures which can be rather easily produced with controlled geometrical parameters and investigated as thin film samples (see Figure 1). A lot of efforts were made to find classic quantum effects, to influence the structure, stability and thermodynamic parameters of the chalcogenide material in very thin layers (see for example a review of K. Tanaka [14]), but the applied results are connected to the driven optical and electrical parameters, as well as to the optical recording in nano-multilayers [15]-[17].

Results on optical recording in some new NMLs are presented in this paper and compared with earlier results on the best known Se/As$_2$S$_3$ nano-multilayers.

II. Experimental techniques

Alternating deposition of two different compositions during thermal evaporation (TE) of initial materials from evaporators in a vacuum chamber (chalcogenide glasses A and B or chalcogenide glass and another material like SiO$_x$, Sb) is comparatively the simplest fabrication method of nano-multilayers used in laboratories [15]-[17]. It was first developed in co-operation with Uzhgorod National University, Ukraine and made more precise at the University of Debrecen due to the computer driven evaporation cycles. High quality metal/chalcogenide NMLs were produced this way in Debrecen during the last year. Corning glass 7059, quartz, sapphire or Si wafer are mostly used for substrate. While the stability of the
Figure 1: Nano-multilayer for optical recording.

The modulation period $\Lambda$ is provided by the computer-regulated time of deposition and vapor flow, the preservation of the composition is the bottleneck of this method in the case of multicomponent initial glass or other material, which can disproportionate during evaporation. Better results can be achieved by pulsed laser deposition (PLD) method. We fabricated excellent chalcogenide NML structures last year in co-operation with University of Pardubice, Czech Republic. We used a PLD method, based on KrF excimer laser operating at 248 nm with constant output energy of 250 mJ per pulse, with pulse duration of 30 ns and with repetition rate of 10 Hz [18].

The direct determination of the periodicity, its change during the annealing or illumination of the NML and the estimation of the quality at the same time usually is performed by Low Angle X-ray Diffraction (LAXRD) method. The time dependence of the intensity of the first diffraction pike at the given temperature or illumination intensity may be used for the determination of the diffusion coefficient $D$: it was equal to $1.23 \times 10^{-23}$ m$^2$/s at 360 K. Examples are presented in Figure 2. The modulation periods $\Lambda$ are usually in the 3-10 nm range, the total thickness of the NML is between...
The problem of the structural stability (at interfaces and at in the sub-layers as well) is crucial for any superlattice and NML. But for the NML it appeared as a source of new optical recording effects [19, 20]. These are accompanied by the changes of optical transmission, reflection, refraction which are measured usually by the known methods of optical spectroscopy of thin films. The local change of the thickness corresponding to the distribution of the illumination at the surface in the appropriate NML samples is easily determined by the AFM measurements [19]. Other optical (Raman scattering [21], luminescence [22]) as well as electrical (DC conductivity, photoconductivity) investigations [23] are often made and analyzed to determine the mechanism of electron processes and of the stimulated structural transformations (interdiffusion, crystallization) in NML.

III. Main experimental results

One of the well known peculiar properties of amorphous chalcogenide layers are the photo-stimulated changes of optical parameters, which in a simplest way are observed as photo-darkening due to the visible light stimulated red shift of the optical absorption edge of the homogeneous layers like As$_2$S$_3$, GeS, AsSe and many others, even of the pure a-Se.

It had appeared that in NMLs more important was the stimulated
mass transport (interdiffusion) across the interfaces. The rate of interdiffusion increases by an order of magnitude if the a-Se/As$_2$S$_3$ chalcogenide-chalcogenide NML is irradiated by laser light ($P \approx 0.8$ W/cm$^2$, $\lambda = 633$ nm). The stimulated interdiffusion usually results in the bleaching of the NML (blue shift of the absorption edge) since the intermixing of the wide- and narrow band gap materials gives a solid solution with a wider band gap in comparison with an initial narrow-gap, active sub-layer. The resulting amplitude relief of optical transmission may be tuned by the selection of the certain pairs of components (see example in Figure 3), some of which were patented [24]. The great advantage of some NMLs with stimulated intermixing effects is the change of the density of the resulting multicomponent material as well as of the index of refraction, what allows in situ recording of amplitude-phase and geometrical surface relief, as it is demonstrated in Figure 4 for a-Se/As$_2$S$_3$ NML. Besides the laser light, interdiffusion may be stimulated by accelerated ions too [25] that broaden the possibility of surface relief fabrication.

Figure 3: The change of the optical transmission relative to its initial value on illumination by green laser diode ($P=0.3$ W.cm$^{-2}$) in Te/As$_2$S$_3$ (1) Se/As$_2$S$_3$ (2) and Sb/As$_2$S$_3$ NML with Sb sub-layer thickness 2.4 nm (3) and 1.2 nm (4).

Figure 4: AFM picture of the surface relief, corresponding to the interference pattern recorded in Se/As$_2$S$_3$ NML.
One more possibility for optical recording arose from the stimulated interdiffusion of metals and chalcogenides in NML [20]-[23]. In this case the role of illumination is reduced mostly to the heating and less to the excitation of the material. The localized enhancement of the diffusion can result very high amplitude (and phase) contrast, which depends on the thickness of the metal sub-layer (see Figure 3). However, it was shown last time, that no essential volume change occurs in Sb/As2S3 NMLs in spite of the excellent amplitude optical relief formation.

The mechanism of the stimulated interdiffusion is tightly connected to the defects of the glass structure. Some conclusions on the type of defects were made on the basis of low temperature photoluminescence investigations in NMLs [22], but more exact models can be developed on the basis of XPS investigations, which are under development.

IV. Conclusion

Nanoengineering of the amorphous chalcogenides, namely the creation of different nanolayered structures opened new possibilities for tuning the stimulated structural changes which in turn can be used for the development of special photosensitive layers or direct, one-step amplitude-phase optical recording, fabrication of special surface relief structures.

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