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Amorphous chalcogenide nano-multilayers: research and development

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Investigations of photophysical processes in amorphous chalcogenide layers were extended during the last two decades towards the nanostructures. Namely the nano-layered films were in the focus of development of new photosensitive, optical recording media. A short review of the progress made in the development of the technology, selection of the components and in the understanding of the physics of stimulated transformations is presented.

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1. Introduction

Chalcogenide glasses are versatile semiconductor and dielectric functional materials, since 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 a number of books and review papers [1-4] and have been applied in devices: electrophotography (Xerox copy machine), X-ray photoreceptors [5], Ovonic switch [6], holographic gratings [7], waveguide sensors [8], all optical switch [9], RW CD [10]. In spite of a wide range of compositions in binary, ternary and more complex systems of chalcogenide glasses [11-13] the problem of smooth or abrupt modification of parameters still exists. These modifications can be performed partially by the special technologies (cooling rate, thin film deposition) or by creating complex artificial structures as it is 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 materials at nano-scale scientists drew attention on amorphous materials. The first was amorphous hydrogenated silicon and similar amorphous semiconductors which served the basis for creation of amorphous superlattices [14-16]. It should be better to use definition “multilayers” for amorphous materials instead of ”superlattice” due to the number of discrepancies arising from the basic nature of quantum effects in a periodical crystal lattice and from the disordered structure of amorphous films.

Multilayer structures are the simplest artificial nano-structures which can be rather easily produced with controlled geometrical parameters and investigated as thin films. It is essential, since the changes of the optical parameters (blue shift of the fundamental absorption edge, quantum states, luminescence), as well as of the conductivity, melting temperature (stability) are characteristic and usually examined in nanostructures. Just the change of the conductivity and photosensitivity of the electrophotographic layer was the driving force of the first experiments on the amorphous chalcogenide nano-multilayers which were made in Bulgaria [17,18] and Ukraine [19,20]. Of course, a lot of efforts were made to find classic quantum effects, to influence the structure, stability and thermodynamic parameters of the chalcogenide material in a very thin layers (see for example a review of K. Tanaka [21]), but the applied results up to now are mostly connected to the driven electrical parameters and to the optical recording. The last will be analyzed in more details in this paper.

2. Technology and experimental

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 an other material like CdS, SiO_x, MgF_2, Au, Bi) is comparatively the simplest fabrication method of nano-multilayers (NML) used in laboratories [22, 23]. The quality of the resulting multilayer structure depends on the stability of the modulation period Λ, on the sharpness of interfaces and on the preservation of the given compositions and structure of the sub-layers through the whole multilayer. Of course, the substrate must be as smooth as possible, otherwise the surface roughness will be reproduced in the interfaces and in the whole NML structure. Corning glass 7059, quartz, sapphire or Si wafer are mostly used for substrate. While the stability of Λ is provided by the computer-regulated temperature of evaporators, by the time of deposition, vapor fluence [23] 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 the evaporation. Better results can be achieved by pulsed laser deposition (PLD) method, which was performed first by pulsed evaporation of the glass target by 1.6 ms pulses of Nd-glass laser

(λ = 1.06 μm) [24]. Excellent NML structures were fabricated by 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 [25].

The direct determination of the periodicity, it's 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 peak at the given temperature or illumination intensity may be used for the determination of the diffusion coefficients. Examples are presented in Fig. 1.

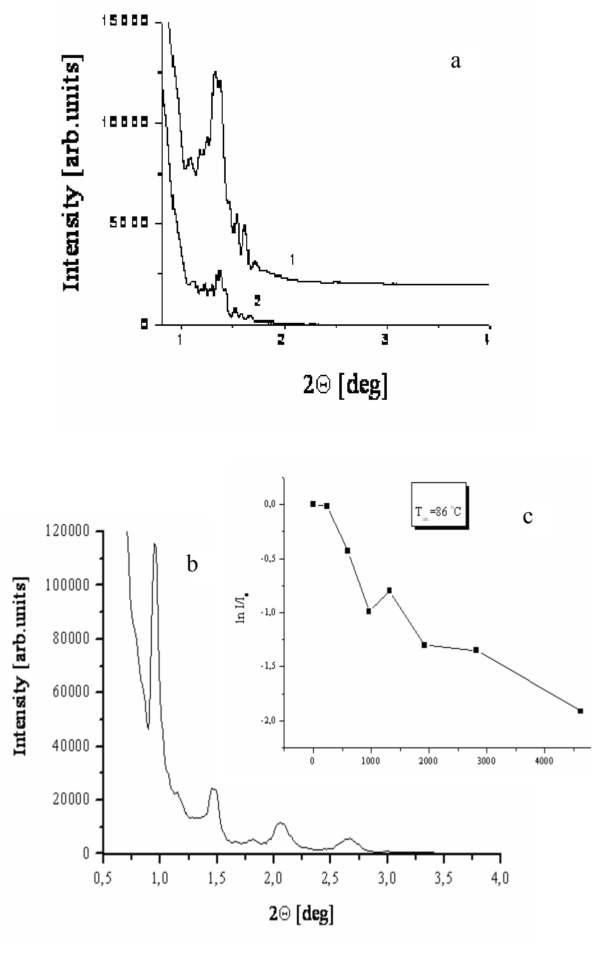

Fig. 1. a) LAXRD spectra of as-deposited (1) and annealed (b) TE a-Se/As_2S_3 NML, b) LAXRD spectrum of the PLD a-Se/As_2S_3 NML, c) Decrease of the first diffraction maximum in Fig. 1.b. with the time of annealing at 86 °C. The estimated coefficient of diffusion $D = 1.23\times10^{-23}$ m^2/s.

The modulation periods Λ are mostly in the 3-10 nm range, the total thickness of the NML is between 0.5-5.0 μm. The problem of the structural stability (at interfaces and at in the sub-layers as well) is crucial for any superlattice including NML. But for the NML it appeared as a source of new optical recording effects [26,27]. 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 [27]. Other optical (Raman scattering, luminescence) as well as electrical (DC conductivity, photoconductivity) investigations are often made and analyzed to determine the mechanism of electron processes and of the stimulated structural transformations (interdiffusion, crystallization) in NML [28-30].

3. Experimental results

As it was mentioned in the Introduction, one of the main result of nano-engineering the chalcogenide glasses was the possibility to change their photoelectrical parameters and to develop new processes of optical recording.

The presence of hetero-interfaces in NML structures made of different compositions like Se/Se-Te, As-Se/Se-Te influence the charge transport and polarization effects, resulting in electrical switching, persistent photoconductivity [30], changes of the drift mobility and I-V characteristics [19]. All of these must be taken into account when developing high-resistance photoconductive layers for electrophotography. Combining wide- and narrow band gap chalcogenide nano-layers in the NML we got highly sensitive structures with a broadened range of spectral sensitivity (see examples in Fig. 2) what was important for the development of IR-sensitive photoreceptor materials.

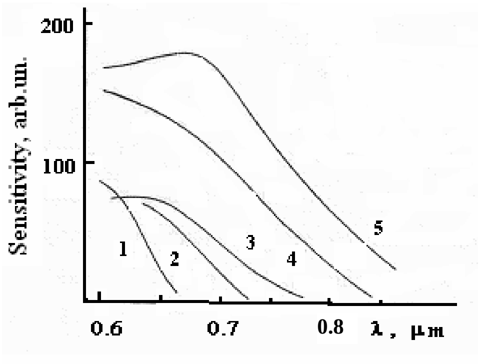

Fig. 2. Spectral dependences of the electrophotographic sensitivity of separate As_6Se_{94} (1), $Se_{90}Te_{10}$ (2) $As_5Se_{85}Te_{10}$ (3) layers, As_6Se_{94} / $As_5Se_{85}Te_{10}$ heterostructure (4) and of the NML from the same semiconductors (5).

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_2S_3, As_2Se_3, AsSe and many others, even of the pure a-Se [20]. It is possible to observe photo-bleaching almost in all of the same compositions if the thermal evaporation conditions are changed towards the higher temperatures, non-equilibrium deposition [31]. It was shown that the photodarkening effect is not essentially influenced by nanostructuring [32] since it depends on the localized, short-range changes of the layered-chainy atomic structure of the glass.

It appeared that more important was the stimulated mass transport (interdiffusion) across the interfaces in the NML and the changes of crystallization process in NML structures. The rate of interdiffusion increases by an order of magnitude if the a-Se/As_2S_3 chalcogenide-chalcogenide NML is irradiated by laser light ($P \approx 0.8$ W/cm^2, λ=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 proper pairs of components (see example in Fig. 3), some of which were patented [33]. The great advantage of proper NML 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 surface reliefs, as it is demonstrated in Fig. 4 for a-Se/As_2S_3 NML. Besides the laser light interdiffusion may be stimulated by accelerated ions too [34] that broaden the possibility of surface relief fabrication.

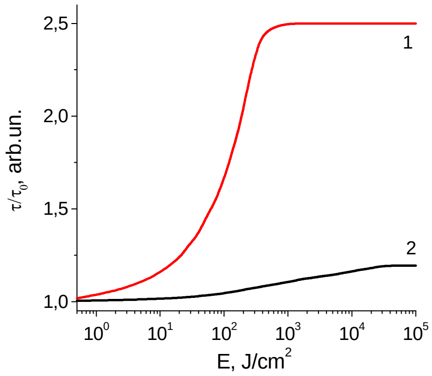

Fig. 3. The change of the optical transmission τ relative to its initial value τ_0 on illumination by He-Ne laser in Te/As_2S_3 (1) and Se/As_2S_3 (2) NML.

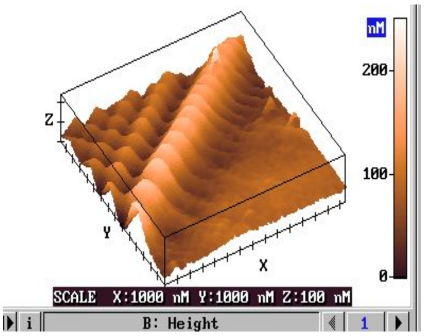

Fig. 4. AFM picture of the surface relief, coresponding to the interference pattern recorded in Se/As_2S_3 (2) NML.

One more possibility for optical recording arose from the stimulated interdiffusion of metals and chalcogenides in NML [35-37]. In this case the role of the illumination is reduced basically to the heating of the material and localized enhancement of the diffusion. Good amplitude-phase reliefs can be produced by this method in Bi (Sb, Ag) NMLs. These can be read out electrically too. Solid phase synthesis of multicomponent, metal-containing glasses and composites also can be performed this way.

If the NML consists of alternating chalcogenide (crystallizing compositions like $Se_{0.5}$ $Te_{0.5}$) and an other material (SiO_x, MgF_2, organics, etc.), which do not form solid solutions due to the intermixing (interdiffusion is not favoured) the crystallization processes may be tuned by the modulation period and illumination or, heating [38]. This processes are interesting for the investigations of basic parameters of phase transitions and also can be used for optical recording.

4. Conclusion

Nanoengineering of the amorphous chalcogenides, namely the creation of different nanolayered structures opens new possibilities for tuning the basic optical parameters and 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 the surface relief structures.

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