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ADP011500 thru ADP011563
LIGHT-STIMULATED STRUCTURAL TRANSFORMATIONS AND OPTICAL RECORDING IN AMORPHOUS NANO-LAYERED STRUCTURES

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The investigations of light-stimulated structural transformations in chalcogenide glasses are expanded towards multilayer structures with nanometer-scale components. The results of optical recording experiments and the new details of the recording mechanisms are reviewed.

(Received June 6, 2001; accepted June 11, 2001)

Keywords: Nanostructures, Structural transformations, Optical recording

1. Introduction

Amorphous semiconductors emerge in a wide class of glasses, amorphous organic and inorganic materials. They are attractive objects for theoretical and applied investigations on structure-dependent optical, electrical and other characteristics in bulk or thin film structures, owing to the existing general problems of ordering-disordering in materials science, charge localisation and transport phenomena or to the applications in optics, optoelectronics [1-3]. Advanced nanotechnologies and nanophysics widely use amorphous semiconductors as basic components in atomic engineering of new materials, electronic devices [4,5]. Amorphous Si, Ge, Se and chalcogenides are the most known and investigated in connection with the problems of tailoring optical and electrical parameters due to the nanometer scaling [6-9]. Experimental investigations are mostly conducted on a superlattice-type structures, which allow us to simplify the sample technology and the analysis of the results [10,11].

Optical recording processes have become of special interest besides usually investigated degradation, shift of the optical absorption edge, luminescence in nanostructures. a-Se/As2S3 nanolayered structures (NLS) seems to be up to now the most interesting for amplitude-phase optical recording in a real time-scale [12,13], while SeTe-containing NLS are promising as photoconductive materials for electrophotography [14,15]. Both electrophotography and amplitude-phase relief formation on a sensitive chalcogenide layer are optical recording processes or non-silver photography, but the first is determined by the light-stimulated electron movement while the last depends on the light- or heat-stimulated atomic displacement, structural transformations within one phase (amorphous-amorphous) or between different states (amorphous-crystalline). The mechanism of these processes may be effectively tailored in nanostructures, thanks to the changes in electron spectra, thermodinamical and mechanical parameters (defect states, temperature of crystallisation \( T_c \), diffusion, stress). Most of them have not been well examined so far. It is the goal of this paper to review the results of experimental investigations of the above-mentioned nanostructures in regard to the well known electrophotography process, structural transformations in As-(S,Se,Te)-type homogeneous layers and to the less investigated interdiffusion processes in amorphous multilayers, all of which can be modified by light-stimulated transformations and used for optical recording.

2. Materials, technology and investigation methods

According to the known publications and experience in amorphous NLS production the existing vacuum technology seems to be the most reasonable both in quality and in price. Cyclic magnetron sputtering or thermal evaporation can be used first of all [9,16-18], but pulsed laser or e-
beam evaporation are also applicable for chalcogenides and other amorphous semiconductors. The quality of NLS in all cases is comparable with the results, obtained by plasma CVD for a-Si:H NLS [5]. Small-angle X-ray diffraction (SAXD) and TEM investigations support the conclusion that 3-10 nm layer spacing (periods $A=6-20$ nm) may be kept up to the total thickness of NLS $d=0.5-4$ $\mu$m with 0.5-2 nm thick transition layers in the interfaces for different types of combined materials. Of course, it is difficult to imagine such amorphous nanolayered structure as ideal crystalline superlattice like those produced by MBE. Most likely they are well correlated layers, the external surface of which has an average roughness about 0.5-1 nm, as measured by AFM on NLS, deposited from different chalcogenide glasses (ChG) onto Si-wafer, Corning 7059, sapphire substrata.

Structural investigations are usually provided by HRTEM (cross-sections) and SAXD, but optical (Raman scattering, visible- or IR-transmission spectra and optical recording) and electrical measurements (conductivity) are also good indirect methods for monitoring structural changes (crystallisation, interdiffusion) in NLS. Since we are interested in light-stimulated structural transformations, comparison must be done between the results, obtained at different radiation energy densities on the NLS surface and at the simple thermal treatment, annealing. Combining the above-mentioned direct and indirect methods of structural investigations the reliable information can be obtained about the complex changes in optical, electrical, geometrical parameters and the structure of NLS, since optical image relief depends on all of these parameters.

Most of our optical recording experiments were performed with He-Ne laser ($\lambda=0.63$ $\mu$m, output capacity density $P=0.8$ W/cm$^2$), but Ar-ion laser ($\lambda=0.51$ $\mu$m, $P\approx$50 W/cm$^2$) and even pulsed nitrogen laser ($\lambda=0.32$ $\mu$m) or AlGaAs LEDs were used in optical recording experiments.

### 3. Optical recording processes

Non-silver photography or optical recording processes may be realised in amorphous chalcogenides both in the form of electrophotography due to the charging-optical discharging or in the form of amplitude-phase optical relief formation due to the light-stimulated structural transformations. Electrophotographic recording mode is well investigated and applied in copying machines, laser printers in which a-Se-based photoreceptors were used besides novel organic materials. Expanding the electron transport investigations in amorphous materials, especially the application possibilities of ChG, electrophotographic recording mode was performed on Se$_x$Te$_{1-x}$ containing NLS [14,15] and used for determination of the influence of multiple heterostructure formation on the sensitivity, discharge processes. It was established that combining narrow- and wide-gap ChG in a periodical structure Se$_x$Te$_{1-x}$/As$_y$Se$_{1-y}$ ($0.6 \leq x \leq 0.95$, $0.06 \leq y \leq 0.5$) the total sensitivity may be increased up to one-two orders of magnitude in comparison with a homogeneous layer of mixed composition, especially in the near-infrared spectral range (see for example Fig.1). The dark decay of the surface potential slows down while the light-stimulated discharge accelerates, the drift mobility of holes increases [19].

Additional tuning of these parameters is possible by step-by-step annealing, which enhances interdiffusion and leads to the formation of multiple heterostructures with variable bandgaps up to the total intermixing of NSL components [11]. Thus NLS creation from appropriate photoconductive ChG and additional stimulated structural transformations in it are effective methods for tailoring the parameters of photoreceptors for electrophotography [14].
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As far as the interdiffusion is enhanced by thermal annealing, optical recording of bits or amplitude-modulated image relief ($\Delta \alpha$, $\Delta R$) may be realised on the same or similar NSL due to the heating by the focused light beam. Moreover, the method may be expanded to the wide class of effectively intermixing materials, for example Si/Ge NLS [18]. The problem lies in the stability of the structure in the dark at the given temperatures, i.e. triggering of the diffusion is necessary for wide applications, since the sensitivity of the process does not differ essentially from the known process of laser-induced amorphisation-crystallisation in Te-containing ChG films. It was supported by our experiments on a number of Te-based ChG NLS.

The main attention in our experiments was devoted to the optical recording due to the pure light-stimulated effects. Investigations were performed in NLS both in a simple amplitude-modulation mode ($\Delta \alpha$, $\Delta R$) and in a phase-modulation mode, which was realised in a holographic experiment. The first is an easy method to control the type (photo-darkening, photo-bleaching), sensitivity (usually the exposition in $\text{J/cm}^2$, which is necessary for achieving certain contrast of $\Delta \alpha/\alpha$, $\Delta R/R$), dynamic range of stimulated changes.

![Spectral dependence of electrophotographic sensitivity](image)

**Fig. 1.** Spectral dependence of electrophotographic sensitivity of Se$_{0.3}$Te$_{0.2}$/As$_{0.06}$Se$_{0.94}$ NLS (1) and of the homogeneous multicomponent layer of the same composition (2).

![Optical gap as a function of layer spacing](image)

**Fig. 2.** The optical gap $E_g^*$ as a function of layer spacing in a-Se/As$_2$S$_3$ NLS.
Since the changes in $\alpha$, $R$ and $n$ are connected in semiconductors [1,20], the more complete information about the light-stimulated structural transformations in NLS may be obtained from writing-readout-erasing experiments. The latter were investigated mostly in a-Se/As$_2$S$_3$, AsSe/As$_2$S$_3$, As$_2$Se$_{1-x}$/Se$_x$Te$_{1-y}$ NLS due to their sensitivity at the He-Ne laser radiation wavelength. In general, it is important to adjust the optimal spectral range of sensitivity to the recording laser-light wavelength. It was established for ChG NLS that the fundamental absorption edge shifts towards the increasing $E_g$ with decreasing layer spacing, i.e. modulation period $A$. This shift is well-pronounced for $A<14$ nm (see, Fig.). So the NLS with As$_2$S$_3$ or other wide band-gap barriers may be adjusted to the optimum absorption at the recording wavelength. The relative change in $\Delta \alpha/\alpha$, $\Delta R/R$ after maximum illumination is about 30-50%, therefore certain NLS are well applicable for digital optical recording.

There were not large differences between the amplitude (photodarkening) or amplitude-phase (holographic) recording efficiency at 294 K in homogeneous As$_2$Se$_3$, AsSe layers and AsSe/As$_2$S$_3$-type NLS. It is not surprising, since the light-stimulated structural transformations are connected the chalcogen bridge atom and the medium-range order dimensions determine the structural transformations and the resolution limit of optical recording in ChG [14,21]. The interdiffusion, internal stress is small in this type of NLS. Not so in the a-Se/As$_2$S$_3$, As$_2$Se$_{1-x}$/Se$_x$Te$_{1-y}$ and even a-Si/Ge NLS, where photo-bleaching takes place and interdiffusion is intensive. More over, giant deformations (thickness changes up to 4-5%) occurs under the rather low-intensity laser illumination in a-Se/As$_2$S$_3$ NLS, similarly to the expansion effects observed in ChG layers at high-power illumination [22]. The photo-expansion in a-Se/As$_2$S$_3$ NLS is opposite to the small photo-contraction, observed in homogeneous ChG layers and even in a-Se layers [23], and both are applicable for surface relief hologram recording, as it is demonstrated in Fig.3.

![Fig. 3. AFM picture of surface holograms recorded on a-Se layer (left) and a-Se/As$_2$S$_3$ NLS (right).](image)

Interdiffusion, stress relaxation, combined with the known photoplasticity effects in ChG [24] may be involved to the explanation of such expansion effects in NLS. Interdiffusion is better pronounced in Te-based NLS, where it is easily activated [17]. Stress relaxation must also be used for explanation of the short-period grating relaxation under annealing.

The model of the surface grating formation by illumination and its erasing by heating in a-Se/As$_2$S$_3$ NLS was developed. The physical basis of the process is the interdiffusion of a-Se and As$_2$S$_3$ resulting the total volume increase in comparison with a total volume of separated sub-layers. and the effective intermixing of components at short, nanometer-size distances. The concentration profile $C(x)$ along the surface (x-axis) during the interdiffusion in z-direction may be written as:
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\[ C(x) = \sum_{i=0} A_i^0 \exp\left(-D\frac{2\pi i}{\Lambda}\right)^2 t \sin\left(\frac{2\pi i}{\Lambda} x\right), \]  

where \( A_i^0 \) is coefficient, \( D \) - the diffusion coefficient, \( \Lambda \) - the period of the NLS, \( t \) - the illumination time. Thus at the given dependence of \( D \) on illumination \[24\] and the known dependence of the volume (density) on Se concentration in \( \text{As}_2\text{S}_3\)-Se system it is possible to calculate the stimulated thickness changes within one bilayer (see. Fig. 4) and in the NLS. The results fit experimental data of AFM investigations well.

![Fig. 4. The model of surface profile formation during hologram recording: 1- \( t=100 \) s, 2 - \( t=1000 \) s, 3 - \( t=4000 \) s.](image)

The above mentioned distinctive features of light-sensitive ChG multilayers depend on the composition of combined layers and on the nano-periodicity. They must be investigated by the complex of direct and indirect structure-sensitive methods.

The light-stimulated contraction-expansion effects, especially the giant photoexpansion in a-\( \text{Se}/\text{As}_2\text{S}_3 \) NLS are applicable for surface relief hologram recording in the real time scale, without etching. Such relief is stable at 293 K and hard enough to make copies by direct pressing onto the soft polymer.

5. Conclusions

Nanolayered, compositionally modulated structures which consist of combined pairs of light-sensitive and barrier layers made of amorphous semiconductor chalcogenide glasses broaden the possibility of tailoring non-silver photographic processes, optical recording parameters and applications of this class of materials.

Acknowledgements

The author is grateful to colleagues from Uzhhorod and Debrecen Universities for fruitful cooperation and essential contribution into the development of these investigations.
References