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INFLUENCE OF INTERDIFFUSION ON THE OPTICAL AND ELECTRICAL PARAMETERS OF AMORPHOUS CHALCOGENIDE MULTILAYERS

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The influence of light- or thermo-induced interdiffusion on optical and electrical parameters of a-Se/As_2S_3, $As_{0.2}S_{0.8}/As_{0.2}Se_{0.8}$, $Se_{0.6}Te_{0.4}/As_2S_3$, $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$ nanolayered structures was investigated. Correlations between the indirect results on interdiffusion (the sign and value of optical absorption edge shift, the changes of photo- and dark conductivity) and the direct results of X-ray diffraction measurements of the periodicity in the multilayer provide additional possibilities of investigations of diffusion processes, structural stability in light-sensitive multilayers with nano-scale periodicity.

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1. Introduction

Nano-scale engineering is an efficient method for creating new materials and peculiar structures not only from the basic materials of micro- and optoelectronics (Si, Ge, GaAs, etc.) but from amorphous Si, chalcogenide glasses as well [1,2]. Interdiffusion processes in chalcogenide multilayers (ML) provide additional possibilities for optical recording, surface relief formation besides well-known photo-induced effects (first of all photo-darkening or bleaching) [2-4]. The efficiency of these additional components of optical recording depends on the stability of the ML structure, which in turn is determined first of all by interdiffusion. As far as the composition is periodically changing in as-prepared ML and this periodicity, the concentration profiles of components are changing during light- or heat-treatment due to the interdiffusion, correlations can be assumed between the resulting structure, optical and electrical parameters of the multilayer. If so, investigations of these parameters can be used as an additional, indirect method for *in-situ* detection and measurements of stimulated interdiffusion, especially in amorphous nano-modulated semiconductor structures, where classic X-ray diffraction methods are not so efficient. Optimization of such ML structures can be made with regard to the high stability or just instability, which determine the possible application of ML for optical recording [5], electrophotography [6].

2. Experimental technique for preparing multilayers and measuring parameters

Compositionally modulated multilayers were prepared by the method of cyclic thermal evaporation in a vacuum $p = 10^{-4}$ Pa. Multilayers with modulation periods Λ = 5-50 nm and total thickness d = 1-3 μm were deposited onto silica glass or Si-wafer substrata from the proper initially milled As-S(Se) and Se-Te glasses. The periodicity was controlled by the Low Angle X-ray Diffraction (LAXRD) method. AFM pictures of the surface show surface roughness within

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0.5-1.0 nm in different layers, what indicate also the possible roughness of the interfaces, at least in the as-deposited ML.

Initial glasses and the pairs of adjacent layers were selected with regard to the possibility of creation of solid state solutions after the interdiffusion, stimulated by laser illumination (He-Ne laser, $\lambda = 0.63$ μm or Ar-ion laser, $\lambda = 0.49$ μm). Pairs of a-Se/As_2S_3, $Se_{0.6}Te_{0.4}$/ As_2S_3, $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$, $As_{0.2}S_{0.8}/As_{0.2}Se_{0.8}$ were selected as the most suitable and efficient for the diffusion-based optical recording, especially at $\lambda = 0.63$ μm. Important criterions were also low softening temperatures and crystallization abilities, small effects of direct photostimulated structural transformations within amorphous phase.

Optical parameters were calculated from the interference data of transmission spectra according to the method [5] and some ellipsometric control measurements were also made. The changes of optical transmission at the given laser wavelengths were compared with the data on the stimulated shift of optical absorption edges. Optical recording (amplitude or amplitude-phase –type) was performed mostly with He-Ne laser (P_{max} = 20 mW) and the recording efficiency (transmission change or diffraction efficiency of the elemental hologram) was controlled *in situ* or afterwards.

DC conductivity in the dark or photoconductivity was measured in direction parallel or perpendicular to the interfaces of the ML. Graphite, gold or transparent ITO electrodes were used depending on the character of measurements. All measurements were made in a normal atmosphere.

3. Results and discussion

Light- and thermostimulated interdiffusion effects were observed in all investigated multilayer structures (a-Se/As_2S_3, $Se_{0.6}Te_{0.4}/As_2S_3$, $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$ and $As_{0.2}S_{0.8}/As_{0.2}Se_{0.8}$). Diffusion coefficients were in the $10^{-22} – 10^{-23}$ m^2/s range as determined from LAXRD measurements of the changes of the first diffraction peak by the method analogous to Si/Ge superlattices [6]. Some additional attempts for measuring interdiffusion were made by the methods of Raman-scattering and infrared spectroscopy, but the results were not very reliable with regard to the intermixing since the characteristic spectra of separated components in the multilayer and these of the mixed layer were rather similar. Therefore the possible applicability of other optical and electrical methods grows up.

First of all, the optical absorption edge was measured and the results in first approximation were interpreted in the model of effective optical media [6,7], that means averaging of absorption for the total thickness of the multilayer, whereas only absorptive, narrow-bandgap "Well" layers determine the absorption (for example, a-Se in a-Se/As_2S_3 ML), and the contribution of wide-bandgap "barrier" layers (As_2S_3 in a-Se/As_2S_3 ML) is small.

The effective optical bandgap of ML E^*_g was determined from the equation [8]:
$\alpha h\nu \sim (h\nu - E^*_g)^K$, which is valid for a number of amorphous materials in the spectral region of large α ($10^4 \le \alpha \le 10^5$ cm^{-1}), i.e. in the Tauc-region [9,10]. We have determined E^*_g at $K = 2$ and at $\alpha = 10^4$ cm^{-1} like it was applied for amorphous materials in [11]. The typical results for ML with modulation period $\Lambda \cong 8$ nm are summarized in Table 1.

Table 1 Optical and electrical parameters of multilayers.

Type of ML	E^*_g, eV			$\tau/\tau_{0\ max\ ,\ \lambda=0.63\ \mu m}$ %	$\sigma/\sigma_{0\ T=293\ K}$ %
	as prepared	annealed	illuminated	illuminated	illuminated
a-Se/As_2S_3	1.93	1.96	1.95	20	8
$As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$	1.66	1.69	1.70	23	13
$As_{0.2}S_{0.8}/As_{0.2}Se_{0.8}$)	1.91	2.02	1.96	150	-
$Se_{0.6}Te_{0.4}$/ As_2S_3	1.71	1.81	1.82	67	18

It was established, that the decrease of modulation period Λ below 10 nm or of the thickness d_w of the "well" layers below 5 nm at the constant Λ leads to the increase of E^*_g, for 0.01 – 0.08 eV

(see Fig. 1) Thus it is possible to operate in a certain limits optical transmission spectra of ML by changing the initial modulation period. The ΔE^*_g shift can be related to the quantum-confinement effect which was supposed in amorphous superlattices [12], but really we have rather some analogy of quantum confinement in small clusters of glass, which form the thin layer in ML.

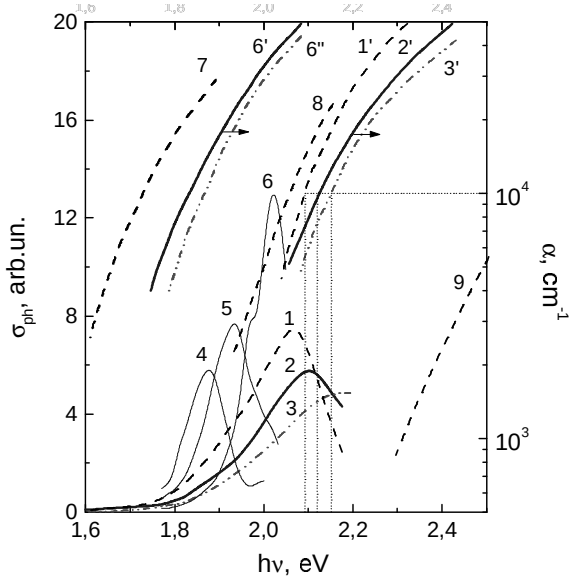

Fig. 1. Spectral dependence of photoconduction σ_{ph} and optical absorption α in a-Se (1,1'); ML a-Se/As_2S_3 before (2,2') and after illumination during 15 min (3,3'); ML $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$ ($\sigma_{ph} \times 3$) with modulation period $\Lambda = 80$ nm (4), 15 nm (5), 10 nm (6, 6') before illumination and (6'') after illumination, and absorption edges in homogeneous as-deposited $Se_{0.8}Te_{0.2}$ (7), $As_{0.06}Se_{0.94}$ (8), As_2S_3 (9) layers.

Light- and thermostimulated interdiffusion effects are similar in all investigated ML [13]: the optical absorption edge shifts towards higher energies (bleaching) for 0.01 – 0.12 eV. The corresponding relative transmission τ/τ_0 increase and the reflection R/R_0 decrease at $\lambda = 0.63$ μm was about 20-50 %, as it was shown also in [2]. The refractive index n decreases for 0.03 – 1.68 %. Bleaching in ML can be explained by the creation of more strong bonds [14] between the components due to the interdiffusion and formation of continuous rows of ternary solid solutions.

Spectral dependences of photoconductivity, its maximums and shifts due to the change of modulation period correlate well with optical absorption, E^*_g in ML (see. Fig. 1). If both ML components initially are photosensitive, in different spectral regions, the resulting photoconduction of ML grows up and the maximum shifts according to the E^*_g (see the example of $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$ in Fig. 1). Thus, smooth tuning of the photoconductivity spectra and enlarged photosensitivity can be realized in such types of amorphous ML by varying initial modulation period and/or by additional light- or thermoinduced interdiffusion in the given structure. The nano-scale modulation period is essential, since only at this dimensions the diffusion process, the intermixing is efficient in the time-scale of the real experiment [3,15]. The presence of energy barriers at multiple interfaces promotes some charge carrier separation, increasing lifetimes and enhanced photoconduction.

Simple model calculations of the resisitivity of ML in directions parallel and perpendicular to interfaces show the increase or decrease of conductivity, respectively, during the interdiffusion, because of the changing thickness of components and creation of solid solution. Good correlation between optical and electrical changes were observed in all investigated MLs. An example for $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$ is presented in Fig. 2. Note that all light-stimulated effects were measured at intensities $P < 1$ W/cm^2, i.e.in a linear region of intensity – effect dependence, where non-linear heating effects of the focused laser beam are negligible [16].

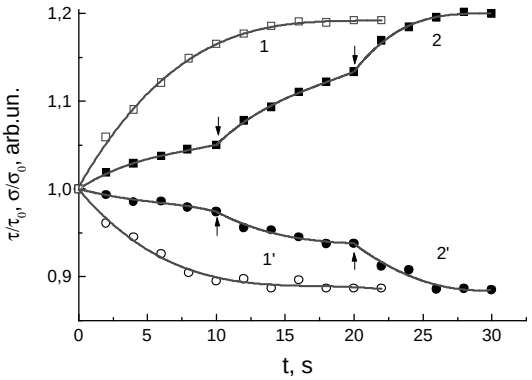

Fig. 2. Relative optical transmission change τ/τ_0 (1,2) at λ = 0.63 μm and the change of dark conductivity σ/σ_0 at T = 293 K (1',2') on the time of illumination at λ = 0.63 μm in ML $As_{0.06}Se_{0.94}/Se_{0.8}Te_{0.2}$: 1,1' – P = 0.5 W/cm^2, 2,2' – P = 0.125 W/cm^2 (at the first step, and intensity is doubled at the points marked by arrows).

4. Conclusions

Amorphous chalcogenide multilayers with nano-scale modulation period show certain analogy with quantum confinement effects of blue- shift in optical and photoconduction spectra. Absorption edge, the maximum of photoconduction and the dark conductivity as well in ML can be tuned by light- or thermally induced interdiffusion, as far as solid solutions can be formed from the components of adjacent layers. The changes of optical, electrical and photoelectrical parameters during the interdiffusion correlate rather well and, therefore, they can be used for indirect measurements of interdiffusion.

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