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Interface effects on the nonlinear optical properties of thin films

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Abstract. The optical nonlinearity of low-dimension structures is studied in the self-effect case at a wavelength of 630 nm in a range of light intensities below 0.1 W/cm^2 by waveguide methods. Common tendencies in relationships between intensity of light and optical properties of multilayer structures and semiconductor-doped glass films are detected. It is shown that the state of interfaces determines the character of optical nonlinearity.

Key words: interface, optical nonlinearity, waveguide

1. Introduction

Thin-film waveguide structures containing materials, whose refractive index depends on the light intensity (Stegeman and Seaton 1985), can find applications in optical signal processing devices (Gibbs 1988). An interesting feature of these structures is the power dependent attenuation of guided modes (Jakubczyk *et al.* 1987; Pal 1993). In this respect, low-dimension structures including thin-film multilayer structures are of considerable interest. The refractive index and the absorption coefficient of these structures are intensity-dependent because of periodicity of their optical properties in the light propagation direction (Gaponenko 1998).

In this paper the nonlinear optical properties of semiconductor-doped glass films and multilayer structures are studied by waveguide methods.

2. Experimental details

Thin-film structures were obtained by RF sputtering of semiconductor-doped glasses (SDG) and by an alternative sputtering of conducting and dielectric materials. Lithium niobate and tin dioxide were used as conductors, quartz glass was used as an insulator. In multilayer structures the layers of quartz glass, lithium niobate, and tin dioxide had thickness of 70, 50, and 10–80 nm,

and refraction index of 1.476, 2.16, and 1.99, respectively. The thickness of sputtering films was monitored by deposition time. A total thickness of the thin-film structures did not exceed 1.5 μm.

When fabricating the multilayer structures thin dioxide layers were prepared by sputtering of ceramic target and lithium niobate layers were made by sputtering of monocrystalline target. Oxygen content of the sputtering atmosphere was varied from 10–20 vol% in the Ar–O_2 mixture. The SDG films were obtained by sputtering of an OS12 glass target (CdS_xSe_{1-x}-doped glass) in an argon atmosphere. All films were deposited on quartz glass substrates at pressure 10^{-3} Torr. The substrate temperature did not exceed 190°C.

Optical parameters of thin films (the refraction index n and the absorption coefficient k) have been measured by means of a prism-coupling technique for a wavelength of 632.8 nm. Using a prism coupler, we excited a waveguide mode in the thin-film structure and measured the spatial distribution of intensity of the light beam reflected from the prism-coupler base (Fig. 1a, curve 1). This intensity distribution was registered by a matrix photodetector placed in a focal plane of a lens. In this way we registered an angular Fourier-spectrum of the reflected light beam. After processing the obtained distribution we could reconstruct real and imaginary parts of the mode propagation constant h ($h = h' + ih'', h' = \mathrm{Re}\, h, h'' = \mathrm{Im}\, h$) (Red'ko *et al.* 1994). The refraction index, the absorption coefficient and the thickness of the film can be determined from h of two guided modes (Sotsky *et al.* 1999).

The nonlinear refractive index n_2 and the absorption coefficient k_2 were measured by waveguide method in the self-effect case at a wavelength of 632.8 nm. Changes in the distribution of intensity of the light beam, reflected from the prism-coupler base in exciting a guided mode, is a result of gradually increasing of the incident light beam intensity of a He–Ne laser (Fig. 1a, curves 1–3). Curve 1 describes the case, when the intensity of the probing light beam was reduced as much as possible by ND filters and was about 0.5 μW. At this level of power, the photo-induced changes in films by red light were hardly observed. The incident light intensity was changed in the range of 0.5–500 μW. The radius of the beam on the prism base did not exceed 200 microns. Complex nonlinear parameter of the waveguide was determined from changes in the spatial intensity distribution. The nonlinear index n_2 and coefficient k_2 were determined after calculations of the refraction index, the thickness of the film, the complex nonlinear parameter and a field distribution of a guided mode (Sotsky *et al.* 1994).

3. Results and discussions

Previous reports (Sotsky *et al.* 1994, Khomchenko 1997) showed a strong nonlinear dependence of optical parameters of As_2S_3 and ZnSe thin films on

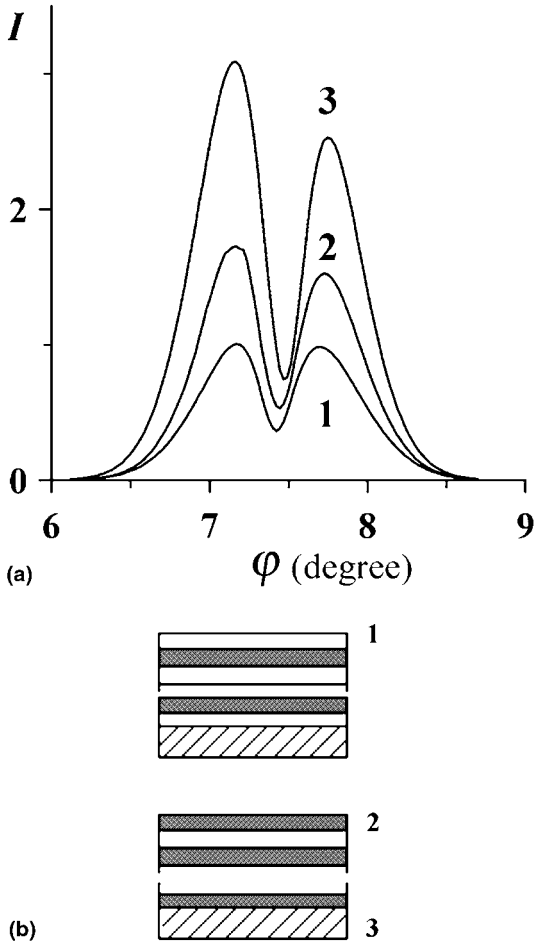

Fig. 1. Changes in the angular Fourier-spectrum (a) of the light beam, reflected from the prism-coupler base at excitation of a guided mode in the thin-film structures (b), caused by increasing of the light intensity ($I_3 > I_2 > I_1$).

the incident light beam intensity in a range below 0.1 W/cm^2. For the As_2S_3 film, the measured magnitude of n_2 was found to be 2.65×10^{-3} cm^2/W. In this case, variations of the optical parameters caused by an increase in the film's temperature due to light absorption ($\sim 10^{-8}$) were much smaller than the registered change in the refraction index. It confirms a nonthermal origin of the optical nonlinearity being observed. An effect of the surface and interfaces was assumed to be a possible reason of this phenomenon (Khomchenko 1997). From this point of view it's interesting to try modeling a similar nonlinear media with a large number of interfaces by preparing a multilayer structure. We have made multilayer structures in which a waveguide layer was surrounded by materials with different optical parameters. Two kinds of

multilayer structures, presented in Fig. 1b, were deposited on the quartz glass substrate 3 (structure 1: 'insulator (1)–conductor (2)–insulator', and structure 2: 'conductor–insulator–conductor'). Both structures were made at identical conditions during the same sputtering process by alternative deposition of lithium niobate and quartz glass and contained eleven layers. The first structure consisted of five layers fabricated by sputtering a lithium niobate target and six layers of quartz glass, on the contrary, the second one consisted of six and five layers, respectively. The conducting layers are isolated from each other by SiO_x layers. Fig. 2 shows h' as a function of the incident light intensity I for these structures. Here and below h' relates to the measurable synchronous angle φ of excitation of a guided mode as $h' = k_0 \cdot n_p \cos \varphi$, where n_p is the refraction index of the prism coupler, k_0 is the free space wave number. In the linear case h' is the real part of the propagation constant of the guided mode. The represented functions are nonmonotonic and have complex behavior. Moreover, $h'(I)$ functions have five and six peaks for structures having five and six lithium niobate layers, respectively.

Similar functions for a multilayer lithium niobate structure having three conducting layers are presented in Fig. 3. In this case the dependence of the integrated reflection coefficient on the incident light intensity had also non-monotonous behavior, as it is shown in Fig. 2 (curve 3). The diameter of the

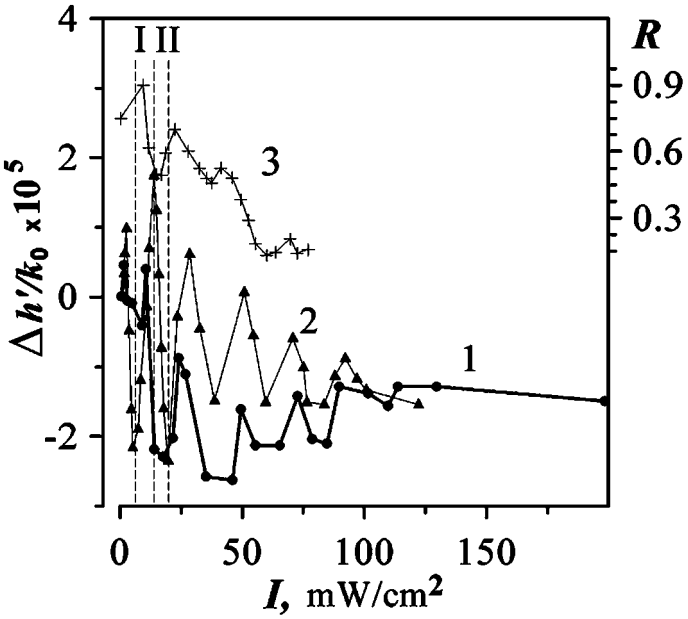

Fig. 2. Variations of the real part of the mode propagation constant h' (curves 1, 2) and the integrated reflection coefficient (curve 3 for structure 2 with three conducting layers) as function of the incident light beam intensity I for the fundamental guided mode of the multilayer structures.

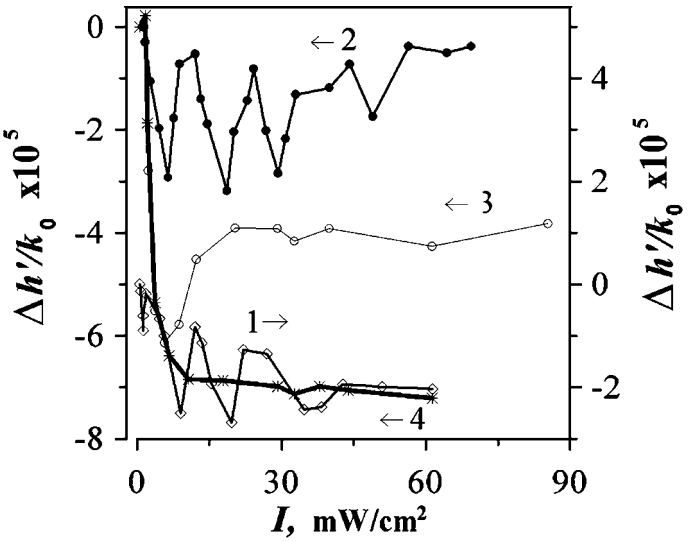

Fig. 3. Intensity dependence of h' for the multilayer structure containing (1) three lithium niobate layers, (2) three and (3) one tin dioxide layer in air, and (4) water vapors.

incident light beam was 290 microns. When exciting guided modes of higher orders and various polarizations in the structure, similar function behavior was observed, too.

Using results of processing the changes in the registered signal form during gradual augmentation of the incident light beam intensity, we determined the nonlinear constants n_2 and k_2 in different intensity ranges: $n_2^{(\mathrm{I})} = -2.1 \times 10^{-3}$ cm^2/W, $k_2^{(\mathrm{I})} = 5.1 \times 10^{-3}$ cm^2/W, $n_2^{(\mathrm{II})} = 3.1 \times 10^{-3}$ cm^2/W, $k_2^{(\mathrm{II})} = -6.2 \times 10^{-3}$ cm^2/W (see Fig. 2, curve 2). Large k_2 and n_2 in the low intensity range of light allow to discuss a possible all-optical control in such structures at the light intensity of about 10 mW/cm^2.

One more type of multilayer structure was made by alternative deposition of linear optical materials such as tin oxide (a conductor) and SiO_2 (a dielectric). The thickness of each layer of this structure was about 10 nm and this structure simulated a low-dimension system. The function $h'(I)$ for this kind of multilayer structure containing three layers of tin dioxide isolated from each other by layers of quartz glass is shown in Fig. 3 (curve 2). This function has three clearly seen peaks, too. It follows from the analysis of these curves, that the complex behavior of $h'(I)$ is defined by the number of layers in the specimen. The thickness d_l of the tin dioxide layers was 12, 24 and 36 nm. It's evident that the wider peak of the curve corresponds to the greater layer thickness. The form of $h'(I)$ in the region of the third peak ($d_l = 36$ nm) is similar to that for the thicker film ($d_l = 120$ nm) presented in Fig. 4 (curve 1), i.e. when the layer thickness is more than about 30 nm, we register the nonlinear response from each interface of the layer separately.

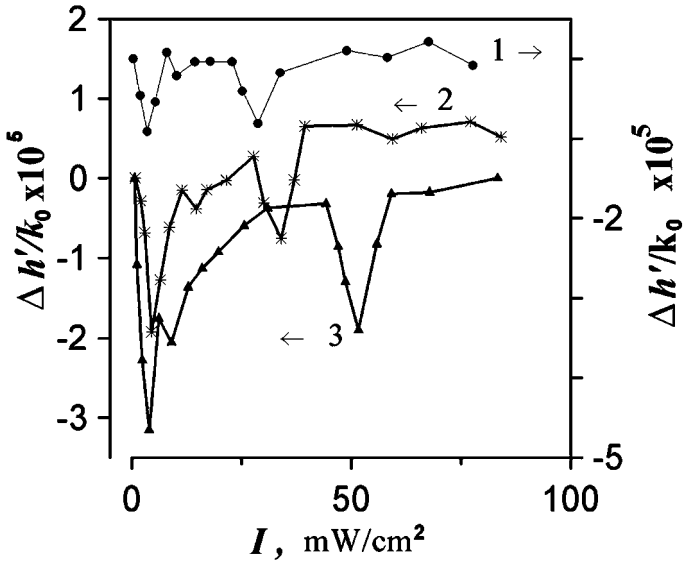

Fig. 4. Variations of real part of the mode propagation constant h' as function of the incident light beam intensity I for the multilayer structures: 'SnO_2 film–quartz glass' (1), 'SnO_2 film–SiO_x film–quartz glass', where the absorption coefficients of SiO_x films are 1.5×10^{-5} (curve 2) and 5×10^{-6} (curve 3).

The nonlinear optical properties of the multilayer structures strongly depended on optical quality of the dielectric layers. Fig. 4 shows the experimental results for three tin dioxide films deposited on different substrates at identical conditions during the same deposition process. Here quartz glass and the structures 'SiO_x film–quartz glass' were used as the substrates. SiO_x films were deposited at various conditions and had a different composition that is why they had different absorption coefficient k. In Fig. 4, curves 2 and 3 correspond to $k = 1.5 \times 10^{-5}$ and 5.0×10^{-6}, respectively. In these structures the layers of quartz glass and tin dioxide had thickness of 1μm and 120 nm, respectively. It is known that even a neutral amorphous substrate affects the thin-film waveguide properties (Khomchenko *et al.* 1993). And in this case the nonlinearity was greater in waveguide structures containing the dielectric film with greater k as a buffer layer between the substrate and the waveguide.

These results show that the interfaces define a nonmonotonic intensity dependence of the thin-film optical properties.

If the origin of optical nonlinearity is associated with the modification of surface states, the behavior of $h(I)$ can be changed by pumping of a gas in the thin film surrounding. The opportunity of realization of such an experiment is stipulated by the fact that at each internal reflection in the waveguide interference between the incident and reflected internal beam creates a non-propagating standing wave, which is perpendicular to the reflecting surface.

The energy associated with this wave tails out into surroundings where it can interact with gas molecules. Chemisorption of a gas on a semiconductor, in particular, results in a change of the power states in the band gap (Kiseljov *et al.* 1986). To make this experiment, the waveguide structure consisting of silicon dioxide and tin dioxide films, which were successively deposited on the base of the prism coupler, was fabricated. Since water vapor actively saturate levels of surface states (Madan *et al.* 1988), we expected the observed decrease in the absorption (and the increase in h') to be suppressed in the film in the water vapor atmosphere.

The results of these measurements in the water vapor atmosphere and in air are presented in Fig. 3 (curves 3, 4). It can be seen that the effect of decreasing the refractive index (and increasing the film absorption) in the range of low intensities of the incident light was present in both cases, but a bleaching of the film in the water vapor atmosphere was not observed. Thus, our assumption that interfaces affect nonlinearity of the multilayer structure optical properties is proved to be quite correct.

The same behavior of the intensity dependencies of optical properties was also observed in thin films obtained by sputtering of semiconductor-doped glasses (Fig. 5) where a complex shape of $h'(I)$ is distinctly seen and the magnitude of its variations greatly exceeds the measurement error ($\delta h' =$

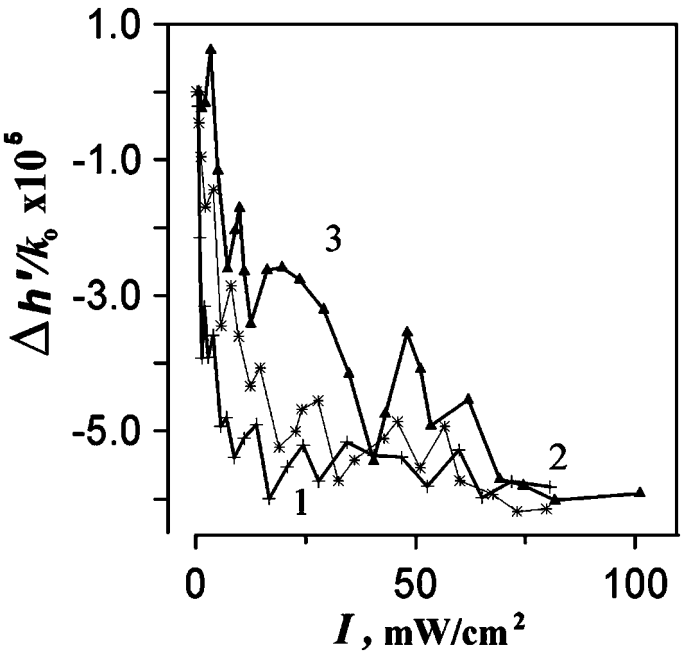

Fig. 5. Changes in parameters of the thin-film waveguides obtained by sputtering of semiconductor-doped glasses versus the incident light intensity I: (1) before, and (2) after thermal annealing and deposited at the substrate temperatures of (1) 140, and (3) 190°C.

5×10^{-6}). It should be noted here that in this case a common tendency of decreasing h' and the absorption is observed.

The foregoing arguments can be applied to the structures from SDG, too. But in this case the surface of the semiconductor crystallite embedded in the glass matrix should be consider as the 'semiconductor–dielectric' interface. By analogy to the multilayer structures we can assume that a greater width of peaks in $h'(I)$ corresponds to a greater crystallite size (compare with Fig. 3, curve 2).

Optical nonlinearity in materials of this kind is defined by semiconductor crystallites embedded in a glass matrix (Gaponenko 1998). Optical properties of SDG depend on the crystallite size, which can be varied by thermal annealing or the deposition conditions. That is why thin-film waveguides from these glasses were heated in vacuum for 4 *h* at temperature of 500°C. The results of measurements of the waveguide parameters before and after annealing are presented in Fig. 5. Just after deposition the statistical size of the crystallites in the films was approximately identical (approximately identical width of peaks on curve 1). After annealing the size of the crystallites changed together with their size distribution (curve 2). The increased temperature of the substrate during deposition resulted in the same changes (curve 3).

Some models have been offered to explain the entire set of phenomena occurring under irradiation of CdS_xSe_{1-x}-doped glasses. One of them considers the escape of an electron from the crystallite into the matrix and the subsequent trapping of the electron on localized states in the band gap of the glass. The filling of localized levels in the glass matrix induces absorption in the impurity-band channels, which results in the appearance of additional absorption in the visible range of the spectrum (Grabovskis *et al.* 1989).

The analysis of our experimental results and results of other researchers (Andriesh and Chumash 1998) show that the photo-induced change in optical properties of the thin films is a result of some photoelectronic effects. Its origin is speculated as a modification of surface states in the band gap. Apparently, the excited mode propagates in all layers of the thin-film structure and the field distributions of the mode at various intensities of the light beam ($I_3 > I_2 > I_1$ – see Fig. 1) are identical (at least, with small I). But at $I = I_1$ the mode amplitude is so small, that the nonlinear effects are not yet displayed or, more correctly, are not registered by the setup available. While increasing $\boldsymbol{I}$ we begin to register the nonlinear response from one interface, then other, etc. Thus, if $|k_2^{(\mathrm{I})}| > |k_2^{(\mathrm{II})}|$ in the structure, the electron processes involved on each of subsequent interface increase the total absorption in the multilayer structure. Accumulating this effect, the structure tends to increase the absorption coefficient during augmentation of the incident light beam intensity. Otherwise, at $|k_2^{(\mathrm{I})}| < |k_2^{(\mathrm{II})}|$ the effect of film bleaching is observed.

Thus, photo-induced changes of optical properties of multilayer structures and SDG films have a common origin. The decrease in h' in the course of successive increase of the incident light beam intensity corresponds to a decrease in the refraction index of the film material. The behavior of the intensity dependence of optical properties of thin-film structures allows the following assumption to be made. With a large degree of reliability the region of the absorption increase (Fig. 2, section 1) can be related to the trapping of the light generated nonequilibrium carriers on localized states in the band gap of the defective dioxide silicon film. The filling of localized levels produces absorption in the visible range of the spectrum. At the same time the cross sections for the carrier capture by defects change as a result of the charged defect presence near the surface. Also it is necessary to note, that some surface states are not localized, and a part of them participates in recombination processes. The filling of free power levels of surface states stimulates the absorption decrease in films. Then the process of photodarkening in thin-film structures can be interpreted within the two-level power model optical recharging of the localized states in the band gap (Malhotra *et al*. 1991), and the bleaching of films can be explained on the basis of the band-filling mechanism (Gibbs 1988).

Thus, the nonlinear changes in the optical properties of these structures can be a result of photo-stimulated migration of nonequilibrium carriers out of the film volume to the interface, of subsequent capture of electrons in localized states in the band gap as well as the processes of carrier recombination. From our point of view these processes define the nonmonotonic behavior of the intensity dependence of optical properties in these structures.

4. Conclusion

We have studied optical nonlinearity in low-dimension structures in the range of light intensities below 0.1 W/cm^2 at the wavelength of 632.8 nm by waveguide methods based on processing a angular Fourier-spectrum of the light beam reflected from the prism coupler base. Common tendencies in relationships between intensity of light and optical properties of multilayer structures and semiconductor-doped glass films were detected. It was shown that the state of interfaces determines the optical nonlinearity behavior.

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