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Photoinduced changes in optical properties of thin film Ag–PbI_2 bilayer systems

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Optical study results of Ag–PbI_2 bilayer photosensitive systems are presented. A reversible change of the system optical transmittance under consecutive irradiation by light from the PbI_2 absorption and transparence regions has been revealed. The action of linearly polarized light on the samples has been shown to result in formation of periodic diffraction structures. The phenomena observed are considered under taking into account the electron microscopic and electron diffraction studies, the concepts of the optics of granular film and waveguide coatings.

В работе представлены результаты оптических исследований двухслойных светочувствительных систем Ag–PbI_2. Обнаружено обратимое изменение оптического пропускания систем при последовательном облучении светом с длинами волн из области поглощения и области прозрачности PbI_2. Показано, что воздействие на образцы линейно поляризованного света приводит к формированию периодических дифракционных структур. Наблюдаемые явления проанализированы с учетом электронно-микроскопических и электронографических исследований, представлений оптики гранулярных пленок и волноводных покрытий.

It is known [1, 2] that a photographic sensitivity effect is observed in bilayer systems on the basis of polycrystalline layers of some metal halides. This basis of that effect is the photostimulated penetration (photoinduced diffusion) of the metal into the polycrystalline layer. A comprehensive optical, electrical, and structure study has been carried out using the Ag(Cu)–PbI_2 photosensitive system. The photoinduced diffusion in such systems has been shown to result in formation of metal clusters (particles) within the polycrystalline layer volume, first of all, in the areas of extended structure defects (dislocations, pores, etc), as well as to give rise to new chemical compounds under partial deterioration of the initial PbI_2 crystallites. At the same time, it is noted that the photodoping mechanism of the polycrystalline layers is not clear completely. The role of PbI_2 layer in the reversible changes of the optical properties of three-layered Ag–PbI_2-chalkogenide glassy semiconductor (CGS) photosensitive systems [3] and in formation of periodic diffraction structures (PS) [4] is studied only scarcely.

In this work, the photoinduced phenomena occurring in the Ag–PbI_2 bilayer are studied. The samples to be studied were prepared by vacuum deposition (about $6.7 \cdot 10^{-3}$ Pa) onto glass substrates at room temperature. Both "forward" (silver layer onto the substrate) and "reverse" (lead iodide layer onto the substrate) systems were obtained. In the deposition course of the layers, the thickness thereof was monitored photometrically using a He–Ne laser ($\lambda = 633$ nm). After the deposition was over, the thickness of individual layers as well as that of the whole system was determined using the multibeam interferometry [5] to be of 10 to 50 nm. Some structure and optical properties of the systems obtained were mentioned

before [6]. The Ag film exhibits an island (mosaic) structure (the particle size up to 100 nm, the filling factor $q \sim 0.5$) while the PbI_2 layer is polycrystalline, the mean crystallite size being about 50 nm, and texturized, the hexagonal axis is oriented predominantly normal to the substrate. To irradiate the samples, intense coherent laser beams were used, the wavelengths being $\lambda_a = 442$ nm and $\lambda_0 = 633$ nm, as well as a non-polarized quasi-monochromatic emission of a mercury arc lamp at $\lambda = 436$ nm. The samples were irradiated both from the free surface side and from the side of the transparent dielectric substrate.

The optical properties of the thin film systems and the photoinduced changes thereof were studied using the optical transmittance (T) spectra within the 360 to 1100 nm range. Since the bilayer systems loss their photosensitive features rather quickly (10 to 100 h), the studies were carried out using the freshly prepared samples.

Fig. 1 presents experimental and calculated dependences $T(\lambda)$ for the forward system in its initial state and after irradiation with light of various spectral compositions. The calculated dependences were obtained using the known relationships for multilayer interference systems [7, 8] and the optical constants for silver, lead iodide layers as well as for potential interaction products thereof [1, 9–11]. The film system models were considered differing in the silver particle distribution over the lead iodide layer thickness, i.e., with different optical profiles. The PbI_2 layer thickness was taken to be substantially unchanged in the course of its photoinduced doping.

For the bilayer system model consisting of Ag and PbI_2 films with a planar interface, the calculated transmittance dependence differs considerably from the optical spectrum of the initial sample (Fig. 1, curve 1), especially in the long-wave region. It is to suppose that silver penetrates in part the PbI_2 layer already at the sample preparation stage. This process may be favored by the substrate surface roughness, the polycrystalline layer macroscale defects, etc. As a result, the Ag/PbI_2 interface becomes blurred and the silver optical constants become changes considerably. The experimental optical transmittance dependence can be approximated satisfactorily by the calculated one obtained using the known relationships of the granular film optics [12]. The calculated curve 1′ (Fig. 1) is obtained under supposition that the initial Ag–PbI_2 system contains a thin interlayer of disperse silver consisting of small (~10 nm) spherical grains surrounded with lead iodide (the bidimensional colloid model). A certain misfit between the experimental and calculated $T(\lambda)$ dependences in the short-wave region seems to result from the fact that the calculations did not taken into account the change in the sample optical properties associated, in particular, with the occurrence of hexagonal and cubic silver iodide modifications evidenced by electronographic examination. So, for example, the singularity observed at 420 nm may be due to the exciton state of β–AgI [11].

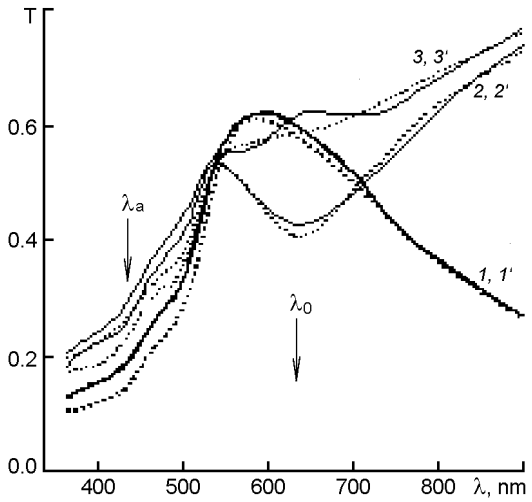

Fig. 1. Spectral dependences of the optical transmittance for a forward bilayer Ag–PbI_2 system. Solid lines show experimental data for: a freshly prepared sample (layer thickness: Ag, about 20 nm, PbI_2, about 27 nm) (1); the sample irradiated with $\lambda_a = 436$ nm light at the energy exposure $H_e = 15$ J/cm^2 (2); that irradiated with $\lambda_0 = 633$ nm at $H_e = 15$ J/cm^2 (3). Dashed lines show calculated spectra for model systems. The individual layer thickness values (from the substrate on, successively): Ag, 16 nm; doped PbI_2, about 1 nm (filling factor $q = 0.45$); PbI_2, about 26 nm (1′); doped PbI_2, about 3 nm ($q = 0.45$); PbI_2, about 24 nm (2′); PbI_2, about 22 nm; Ag surrounded with AgI, about 5 nm (3′).

The optical irradiation of the bilayer systems results in a substantial transformation of the transmission spectra thereof. The irradiation of the samples with the active light at $\lambda_a = 442$ nm (or 436 nm) from the absorption edge of PbI_2 (the transmittance coefficient $\alpha \sim 2 \cdot 10^5$ cm^{-1} [10] and energy exposure $H_e \leq 15$ J/cm^2) causes a band with the transmission minimum at $\lambda = 620$ to

660 nm in the spectra (Fig. 1, curve 2). As is shown in [3, 12], that band is due to the resonasnce absorption in colloidal silver particles occurring in the PbI_2 layer in the course of the metal photoinduced diffusion. The large band width ($\Delta\lambda \approx 60$ nm) evidences a scatter in the silver particle size, shape, and arrangement. The weak minimum near 620 nm is observed also in the freshly prepared samples, thus seeming to evidence the onset of the colloidal absorption development. This is favored by the thermostimulated silver diffusion during its deposition onto the polycrystalline PbI_2 layer.

The calculation presented in Fig. 1 (curve 2′) has been carried out for a model thin film structure that contains in the PbI_2 layer part adjacent to the substrate small spherical Ag grains at the volume filling factor $q = 0.45$. This estimated q value exceeds the volume fraction of macroscale voids in the PbI_2 layer (about 0.2 according to [2]). The filling factor value selected for the calculation is confirmed indirectly by electron diffraction and electron microscopy data that evidence a considerable straining and the crystallite size reduction (about halving) resulting from the irradiation. The structure distortions are possible also due to appearance (at large exposures exceeding 20 J/cm^2) of a new polycrystalline substance, perhaps Ag_2PbI_4 superionic compound [1] with cubic lattice. The photoinduced changes in the structure and chemical composition result in destruction of the excitonic PbI_2 state and thus in disappearance of the 500 nm band (Fig. 1, curve 2).

When the initial forward bilayer systems are exposed to the $\lambda_0 = 633$ nm radiation from the PbI_2 transparence region [10], the transmission spectrum is changed considerably, too, but the colloid band does not appear (Fig. 1, curve 3). The λ_0 light action onto the bilayer systems after a preliminary irradiation with the light from the PbI_2 absorption region results in the disappearance of the colloid band in the spectrum and an enhances transmittance (by about 15 to 20 %). The absorption band disappears also when the initial reverse systems are irradiated. The electron diffraction examination shows that the AgI phase content increases in the irradiated samples. The calculated dependence of the optical transmittance for the thin film system irradiated with the λ_0 light (Fig. 1, curve 3′) has been obtained under supposed silver displacement towards the PbI_2 outer boundary and the filling factor

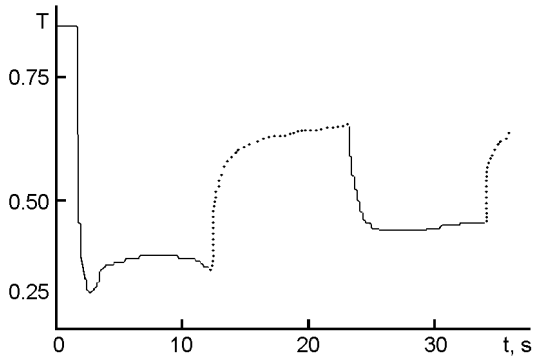

Fig. 2. Photoinduced changes in the optical transmittance at λ_0 in a bilayer Ag–PbI_2 system. Solid lines answer to irradiation with $\lambda_a = 442$ nm light at the energy illuminance $E_e = 1$ W/cm^2; dashed ones, to $\lambda_0 = 633$ nm and $E_e = 6$W/cm^2.

reduction ($q = 0.15$). The dipole interaction between the silver particles surrounded with dielectric AgI envelope was taken into account.

The optical spectrum changes are repeated (at the cycle number exceeding 10) as the bilayer systems are subjected to alternating irradiation with the light from the absorption and relative transparence regions of PbI_2 (Fig. 2). To read the photoinduced changes, an attenuated radiation at λ_0 was used. Some singularities are observed in the time dependence of transmittance during the first several optical action cycles, and then the $T(t)$ kinetics met an exponential law (at irradiation with a strongly absorbable light) and a power one (at irradiation with the λ_0 one) [13].

The results obtained allow to suppose that the observed photoinduced changes in the sample transmittance in the colloid band region are due to reversible processes in the silver particles within the PbI_2 layer (Fig. 2). The AgI photolysis reaction having the photosensitivity threshold corresponding to the energy about 2.75 eV [13] may be of considerable importance in this case. So the irradiation of the initial samples with the λ_0 light favors the Ag penetration into the PbI_2 layer and formation of relatively large silver particles but hinders also the silver iodide formation (the light quantum energy 2.81 eV). The successive irradiation of the samples with the λ_0 light seems to be characterized by the silver particle size reduction in the course of its photoinduced diffusion and the corresponding weakening of the colloid absorption band. In this case, AgI can be formed predominantly at the PbI_2 crystallite boundaries, that is favored by a high concentration of atoms with distorted

coordination and broken lead-silver bonds, i.e., by the presence of a large amount of iodine ions [14]. The action of short-wave light with λ_a causes the AgI photoinduced decomposition, thus giving rise to enlargement of the metal particle and formation of the new ones. The Ag grains of photolytic origin cause an intense absorption band in the optical spectrum. The colloid band shift by about 20 to 40 nm towards longer wavelengths observed under the cyclic light action may evidence a reduction of the dielectric constant in the medium surrounding the silver grains [12]. This reduction is due in part to the AgI content increase as well as to the silver exit onto the free outer surface of the sample. The damping of the reversible photoinduced phenomena is due, first of all, to oxidation reactions occurring in the samples (lead oxide formation is observed), hydrolysis, etc. The sublimation of iodine released under photolysis is possible, too.

Under irradiation of the bilayer systems with linearly polarized λ_0 light, irregular periodic structures (PS) are revealed similar to those observed before in thin film systems on the silver halide basis as well as in three-layer Ag–PbI_2-(CGS) and bilayer Ag(CGS) systems [4, 15]. The PS presence is indicated in the optical transmittance spectrum by a maximum at the λ_0 wavelength (Fig. 1, curve 3), the so-called spectral photoadaptation effect [16]. The PS development was monitored directly in the course of the bilayer system irradiation with the λ_0 laser beam. To that end, the optical recording scheme of the beam diffracted on the PS, the beam being propagated within the substrate and exiting through its butt (only one diffraction reflex was observed). The predominant orientation of the PS lines is parallel to the **E** vector of the light wave, thus indicating that the lines are associated with the excitation of the waveguide TE_0 mode in the PbI_2 layer (the cutout thickness about 19 nm). The PS period determined from the diffraction measurements agrees well with the electron-microscopic examinations as well with the calculated values obtained taking into account the TE_0 mode propagation in a single-layer waveguide [17]. For the sample presented in Fig. 3, the interline distance in the PS is about 410 nm, i.e., it is considerably shorter than the wavelength of the recording radiation. The small particles forming the PS (perhaps the silver metal grains) have the linear dimension of several nanometers and are distributed over the sample surface at the filling factor about 0.15. Some of those form chain-like structures meeting each other at angles near 120°, thus evidencing the particle localization at the boundaries of PbI_2 crystallites. Under further irradiation of the samples with the λ_a light, the PS become degraded; the number of the reversible record/erase cycles for the PS is small (about 3) due to a rapid damping of the TE_0 mode in the samples with numerous structure defects and changed chemical composition. Due to strong damping of the waveguide modes, the PS are not formed also in the case when the initial Ag–PbI_2 systems are irradiated with linearly polarized λ_a light from the PbI_2 absorption region. In this case, the condition $d << \alpha^{-1}$ is not met (where d is the PS period; α, the PbI_2 absorption coefficient) that, as is shown in [18], defines the PS formation possibility.

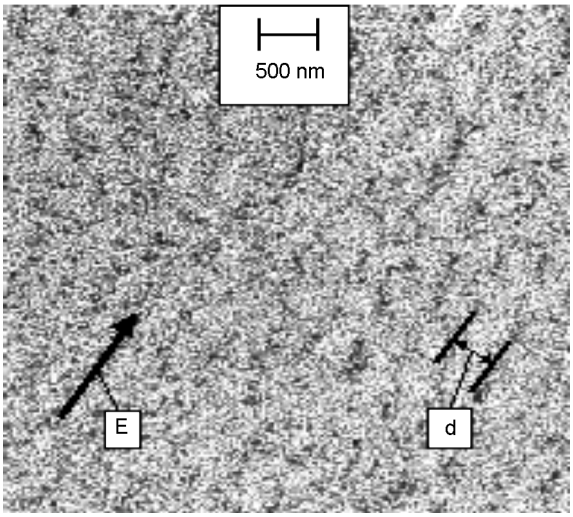

Fig. 3. Microphoto of a bilayer Ag–PbI_2 system sample irradiated with $\lambda_0 = 633$ nm light. The initial layer thickness values: Ag, about 20 nm; PbI_2, about 27 nm. **E** is the electric field strength of the light wave; d, the PR interline distance (period).

The studies of the bilayer Ag–PbI_2 photosensitive systems allow to conclude that the phenomena of reversible changes in optical properties and PS formation observed before in three-layer Ag–PbI_2-(CGS) are due to a great extent to photoinduced processes occurring within the PbI_2 layer. The results obtained improve the concepts of possible mechanisms of the photostimulated diffusion of metals in polycrystalline semiconductor layers.

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Фотоіндуковані зміни оптичних властивостей тонкоплівкових двошарових систем Ag–PbI_2

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В роботі наведено результати оптичних досліджень двошарових світлочутливих систем Ag–PbI_2. Виявлено оборотну зміну оптичного пропускання систем при їх послідовному опроміненні світлом з довжинами хвиль із ділянки поглинання та ділянки прозорості PbI_2. Показано, що вплив на зразки лінійно поляризованого світла призводить до утворення в них дифракційних періодичних структур. Явища, які спостерігаються, проаналізовано з урахуванням електронно-мікроскопічних та електронографічних досліджень, уявлень оптики гранулярних плівок та хвилеводних покриттів.