Functional Materials 13, No.2 (2006)

Photoinduced phenomena in thin-film Cu–PbI_2 and Cu–PbI_2-chalkogenide glassy semiconductor systems

V.V.Mussil, E.T.Lemeshevskaya, V.V.Pilipenko

National Technical University "Kharkiv Polytechnic of Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

Received September 14, 2005

Results of photoinduced processes study in two-layer Cu–PbI_2 and three-layer Cu–PbI_2-chalkogenide glassy semiconductor (Ge–As–S) systems are presented. Reversible changes of optical transmittance in Cu–PbI_2–Ge–As–S systems under consecutive irradiation with different wavelength light (442 and 633 nm) have been found. It has been established that irradiation of the systems with linearly polarized weakly absorbed light results in formation of periodic diffraction structures. The phenomena observed have been considered taking into account the Cu photodiffusion processes, formation and degradation of small metallic particles in the PbI_2 layer and the light waveguide propagation in the film systems.

Представлены результаты исследования фотоиндуцированных процессов в двух- и трехслойных системах Cu–PbI_2 и Cu–PbI_2-халькогенидный стеклообразный полупроводник (Ge–As–S). Обнаружены обратимые изменения оптического пропускания систем Cu–PbI_2–Ge–As–S при последовательном воздействии на них излучения с различными длинами волн (442 и 633 нм). Установлено, что облучение систем слабопоглощаемым линейно поляризованным излучением приводит к формированию в них периодических дифракционных структур. Наблюдаемые явления проанализированы с учетом процессов фотодиффузии Cu, образования и разрушения мелких металлических частиц в слое PbI_2 и волноводного распространения света в пленочной системе.

The action of a photoactive optical radiation on metal-semiconductor thin-film systems is known to result in the metal penetration into the semiconductor (so-called photodiffusion) [1, 2]. This phenomenon is characterized by a number of parallel simultaneous processes accompanied by changes in the system structure and physico-chemical properties, including the optical ones. Reversible changes of optical properties can be realized in light-sensitive Ag–PbI_2 systems as well as in layered ones consisting of silver and a chalkogenide glassy semiconductor (CGS) based on Ge, As(P), and S(Se) compounds with a polycrystalline PbI_2 interlayer [3, 4]. It has been shown that as such systems are exposed to monochromatic linearly polarized light, the waveguide modes and diffraction periodic structures (PS) can be generated.

The photostimulated of metal-semiconductor interaction was studied before mainly in systems containing a silver layer. Those systems are characterized by a very high chemical and thermal stability. At the same time, as is noted in [2], photosensitive systems where copper is used as the metal are of interest and promise.

In this work, studied are some features of photoinduced phenomena occurring in a bilayer Cu–PbI_2 system and in a three-layer Cu–PbI_2-CGS one. The layers of those systems were evaporated successively in vacuum ($6.7 \cdot 10^{-3}$ Pa) onto glass substrates (the copper layer adjacent to the substrate) at room temperature. The direct thermal evaporation of copper and PbI_2 as well as a discrete pulse evaporation of the CGS was used. A glassy Ge–As–S system was used as the semiconductor layer. The deposition rate (0.5 to 5 nm/s) as well as the thickness of individual layers and the total film system thickness were monitored photometrically at the laser emission wavelength of 633 nm. As is evidenced by electron microscopy and electron diffraction, this deposition technique results in insular copper films (the average particle size about 100 nm); the PbI_2 layer consists of 2H polytype crystallites of about 50 nm size with optical axis C oriented perpendicular to the substrate; the CGS film is amorphous. The prepared sample thickness was measured using interferometry (multi-beam interferometry and optical transmission spectra in the transparency region). The layer thickness for copper and PbI_2 was 5 to 30 nm and for the CGS, about 100 nm. When selecting the layer thickness, it was taken into account that the samples of photosensitive systems should provide optimum photographic characteristics at the reading emission wavelength (light sensitivity, contrast, etc.). Using the known calculation methods [5, 6], the optical constants, the dispersion and photoinduced changes thereof were determined for the CGS film controls. The transmission spectra of freshly prepared and irradiated samples were measured in the 360 to 1100 nm range. The samples were irradiated by laser sources of $\lambda_a = 442$ nm and $\lambda_o = 633$ nm wavelengths as well as by a mercury arc lamp at 436 nm. Both continuous optical exposure and the intensity-modulated one (modulation period 10^2 to 10^{-2} s) were used. The attenuated λ_o emission from the relative transparency region of PbI_2 and CGS was also used to read the optical transmission changes in the course of the system irradiation.

Figs. 1 and 2 represent the experimental and calculated $T(\lambda)$ dependences for the bilayer and three-layer systems both in the initial state and after irradiation by light of various spectral compositions. The calculated dependences were obtained using the known relationships concerning the optics of multilayer interference systems as well as the classic theory of granular film dispersion [7–10]. Various modeling thin film systems were considered. The optical constants of copper, PbI_2, CGS, and possible interaction products thereof [1, 11–14] were

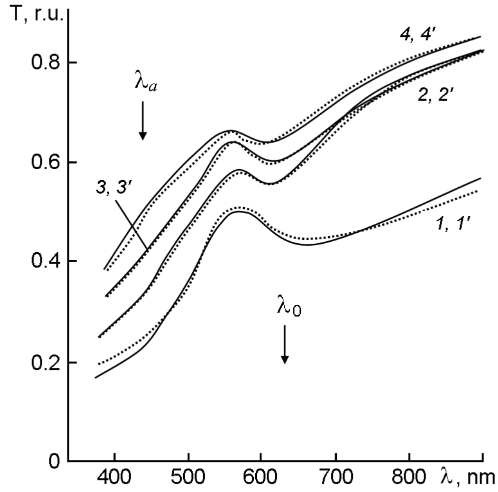

Fig. 1. Spectral dependences of optical transmittance for a Cu–PbI_2 bilayer system. Solid lines — experimental data: *1*, a freshly prepared sample (layer thickness: Cu about 12 nm, PbI_2 about 16 nm); *2*, the sample irradiated at $\lambda_a = 436$ nm and energy exposure He = 15 J/cm^2; *3*, the sample irradiated at λ_o = 633 nm, He = 15 J/cm^2. Dashed lines — calculated spectra for modeling systems.

used in calculations. The intense oxidation processes typical of copper-containing systems were taken into account, too.

The calculated $T(\lambda)$ dependences for the bilayer and three-layer systems with flat layer interfaces are different from the transmission spectra of initial samples (curves *1* in Fig. 1, 2), especially in the long-wavelength region. This suggests that copper penetrates the PbI_2 layer already at the system preparation stage. The penetration may be favored by the substrate surface roughness, macroscale defects of the polycrystal layer, etc. The experimental dependences of the optical transmittance agree satisfactorily with calculated curves (dashed lines *1′* in Figs. 1, 2) obtained using relationships of the granular film optics. The calculations have been done under assumption that in the initial systems, there is a thin interlayer at the Cu/PbI_2 interface consisting of finely dispersed copper particles (<10 nm size) surrounded with PbI_2 (so-called bidimensional colloid model [10]).

Under optical irradiation, the transmission spectra of Cu–PbI_2 and Cu–PbI_2–CGS systems become transformed, that is typical of a direct photographic recording in photodiffusion-based media. As the electron diffraction shows, the photoinduced optical phenomena in thin-film systems are accom-

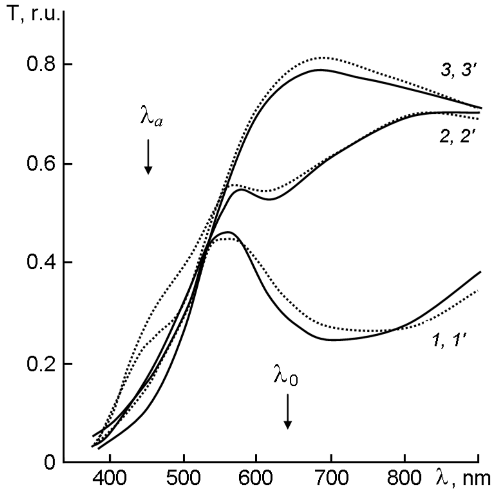

Fig. 2. Spectral dependences of optical transmittance for a Cu–PbI_2–$Ge_{20}As_{20}S_{60}$ three-layer system. Solid lines — experimental data: *1* – a freshly prepared sample (layer thickness: Cu about 18 nm, PbI_2 about 17 nm, $Ge_{20}As_{20}S_{60}$ about 90 nm);); *2* – the sample irradiated at λ_a = 436 nm and energy exposure He = 15 J/cm^2; 3, the sample irradiated at λ_0 = 633 nm, He = 15 J/cm^2. Dashed lines — calculated spectra for modeling systems.

panied by formation of hexagonal and cubic CuI phases while in the bilayer system, copper (CuO and Cu_2O) and lead (PbO) oxide phases are formed. Moreover, the PbI_2 crystal lattice becomes distorted considerably and the crystallite size diminishes.

Irradiation of the thin-film systems with light at λ_a = 442 (or 436) nm from the absorption edge region of PbI_2 and CGS (the absorption coefficients being about 10^5 [14] and 10^4 cm^{-1}, respectively) and at energy exposures $H_e \le 15$ J/cm^2 causes a diffuse band with the transmittance minimum at 610 to 640 nm (curves 2 in Figs. 1, 2). This feature is similar to the resonance absorption band of colloidal silver in silver halide [10] and PbI_2 [3] layers. However, in contrast to the silver-containing bilayer system, the absorption band appears in the Cu–PbI_2 system spectra also in the case of its exposure to the λ_o light from the PbI_2 transparency region [14]. Moreover, that band does not disappear as the system is subjected to consecutive irradiation with different wavelengths. In this case, a shortwave band shift (up to 40 nm) occurs and the transmittance increases within the essentially whole spectral region (curves 2–4 in Fig. 1). Thus, no reversible transmittance changes take place in the Cu–PbI_2 system (curve *1* in Fig. 3).

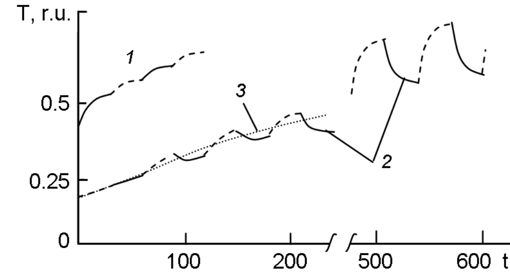

Fig. 3. Photoinduced changes of optical transmittance in bilayer and three-layer systems Cu–PbI_2 (*1*) and Cu–PbI_2–$Ge_{20}As_{20}S_{60}$ (*2*). Solid lines refer to irradiation at λ_a = 442 nm and energy illuminance E_e = 1 W/cm^2; dashed lines, to λ_o = 633 nm, E_e = 6 W/cm^2; Cu–PbI_2–$Ge_{20}As_{20}S_{60}$, continuous irradiation at λ_a = 442 nm and E_e = 1 W/cm^2 (*3*).

The irradiation of the initial three-layer system at λ_o (the film absorption coefficient being about 1 cm^{-1}) causes a considerable transmittance increase (ΔT = 0.5 to 0.6), no colloid band being appeared. Accordingly, the colloid band disappears in the samples irradiated previously with short-wavelength emission (curve *3* in Fig. 2). The changes in the optical spectra are repeated regularly in the three-layer systems subjected to λ_a/λ_o irradiation cycles at the cycle number exceeding 10 (curve *2* in Fig. 3). The reversible T changes can occur against a very long initial section of parabolic kinetics (curve *3* in Fig. 3). This stage is typical of various photographic media where the image is generated immediately in the course of exposure. It is to note that the rate of photoinduced changes is considerably lower (about a decimal order) than that is silver layer containing systems [1, 15].

The studies evidence a complex character of the photoinduced changes in the optical transmittance of Cu–PbI_2 and Cu–PbI_2–CGS thin film systems. That is due to simultaneous running of a series of physicochemical processes. In this connection, the modeling of the phenomena observed and the consideration thereof turn out to be rather difficult. Nevertheless, some suggestions can be formulated. The irradiation of initial Cu–PbI_2 and Cu–PbI_2–CGS samples seems to cause the photostimulated copper penetration into the PbI_2 layer accompanied by the metal segregation in the macro-scale voids of the polycrystalline layer and formation of metal particles [1–3] that absorb the light within a relatively narrow spectral region. Figs. 1, 2 (curves *2′*) present the calculated dependences of optical transmittance obtained for modeling thin-film structures where a part of the PbI_2 layer contains spherical copper grains of about 10 nm size at the volume filling factor of 0.45. When modeling the bilayer systems, the copper oxidation with air oxygen both in the bulk PbI_2 layer and at its free surface was taken into account.

The reversible processes involving the copper particles in the PbI_2 layer and accompanied by CuI photolysis seem to be of considerable importance in the observed photoinduced optical transmittance changes of the Cu–PbI_2–CGS system in the colloid band region. The crystalline CuI phases seem to be formed at the PbI_2 crystallite boundaries, the formation thereof being favored by a high concentration of atoms with distorted coordination and broken lead-iodine bonds [16]. Accordingly, the PbI_2 content lowers. In those processes, the λ_a irradiation favors the photoinduced Cu penetration into the PbI_2 layer and formation of relatively large metal particles and, at the same time, hinders the copper iodide formation (the light quantum energy and the photolysis reaction threshold one are close to one another being 2.81 and ≥2.7 eV, respectively [17]). The copper particle size may be considerably smaller due to formation of CuI phases if the freshly deposited samples are irradiated at λ_o, that is, at low quantum energy (about 1.95 eV). In Fig. 2, curve *3′* is the calculated optical transmission dependence for the three-layer thin-film system obtained under assumption that copper migrates towards the PbI_2/CGS interface and the filling factor is lowered ($q = 0.15$).

In the calculation, the dipole interaction of copper particles surrounded with CuI shells was taken into account as well as the photoinduced change in the CGS optical properties and formation of a granular metal interlayer at the PbI_2/CGS interface. A subsequent short-wavelength irradiation can cause the CuI decomposition resulting in the metal particle size increase and formation of the new particles. The Cu grains of photolytic origin are responsible for an intense absorption band in optical spectrum while the transmittance at the reading emission wavelength decreases respectively (curves *2* and *2′* in Fig. 2).

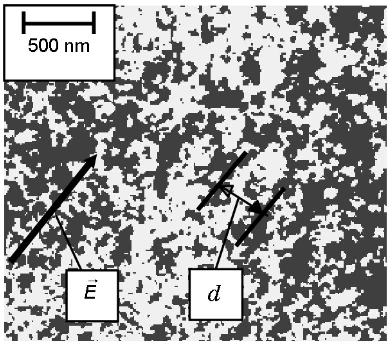

Fig. 4. Micrograph of a Cu–PbI_2 sample irradiated at λ_o = 633 nm. The layer thickness of the initial system: Cu about 12 nm, PbI_2 about 23 nm. **E** is the electric field strength of the light wave; *d*, the PS line spacing (period).

In Cu–PbI_2–CGS systems, the outer amorphous layer seems to act as a protective coating preventing the copper oxidation with air oxygen penetrating through the PbI_2 layer. When the bilayer Cu–PbI_2 are exposed, the copper oxidation hinders to a certain extent the formation of unstable crystalline CuI phases and, respectively, the reversible phenomena. The calculated optical transmittance dependences (curves *2′–4′* in Fig. 1) have been obtained under assumption that a part of the PbI_2 layer contains copper particles surrounded with Cu_2O and a layer of Cu oxidation products is formed at the PbI_2 free surface. It is just the low refractive index values of that layer that can cause the observed optical transmittance increase (so-called clarification effect). The decreased dielectric constant of the medium surrounding the copper particles is testified by the short-wave shift of the colloid absorption band under cycling [10].

Imperfect periodic structures (PS) similar to those observed before in the systems containing a silver layer [3, 18] have been found in bilayer and three-layer system samples irradiated with linearly polarized light at λ_o. It follows from microphotos and electron diffraction patterns that the PS are formed by particles of various sizes (10 to 100 nm). In contrast to the silver-containing system case, these particles are not metallic but consist of the copper-PbI_2 interaction products, CGS, and oxides. The PS lines are oriented predominantly in parallel to the polarization plane of λ_o emission. The PS period determined from the diffraction measurements agrees well with the electron microscopy data (Fig. 4 presents a PS microphotography for a Cu–PbI_2 system, $d \approx 320$ nm) as well as with calculated values obtained under taking into account the TE_0 mode propagation in a planar waveguide (single-layer and bilayer for $Cu–PbI_2$ and $Cu–PbI_2$–CGS systems, respectively). In three-layer systems, the refractive index of the CGS layer varies with its chemical composition, thus causing variations in the waveguide mode propagation constant, β and, as a consequence, in the PS period (d being decreased as the refractive index increases, $d = 2\pi/\beta$). The results obtained can be useful in the studies of optical emission interaction mechanisms with various thin-film light-sensitive systems as well as of realization conditions of reversible optical recording, formation of periodic diffraction structures, etc.

References

1. I.Z.Indutny, M.T.Kostyshin, O.P.Kasyarum et al., Photostimulated Interactions in Metal/Semiconductor Systems, Naukova Dumka, Kyiv (1992) [in Russian].
2. M.V.Sopinsky, G.P.Olkhovik, V.P.Sobolevsky, *Optoelektronika i Poluprov. Tekhn.*, 36th Issue, 83 (2001).
3. V.V.Mussil, Ye.T.Lemeshevskaya, V.V.Pilipenko, *Functional Materials*, **11**, 751 (2004).
4. V.V.Mussil, Ye.T.Lemeshevskaya, A.P.Ovcharenko, *Functional Materials*, **6**, 911 (1999).
5. S.P.Lyashenko, V.K.Miloslavsky, *Optika i Spektr.*, **16**, 151 (1964).
6. V.K.Miloslavsky, A.I.Rybalka, V.M.Shmandiy, *Optika i Spektr.*, **48**, 63 (1980).
7. M.Born, E.Wolf, Principles of Optics, Pergamon, Oxford (1964).
8. D.L.Windt, *Computers in Physics*, **12**, 360 (1998).
9. L.A.Ageev, V.K.Miloslavsky, I.N.Shklarevsky, *Optika i Spektr.*, **31**, 1034 (1971).
10. L.A.Ageev, V.K.Miloslavsky, V.I.Lymar‘, *Zh. Prikl. Spektr.*, **73**, 331 (1992).
11. I.N.Shklarevsky, A.I.Usoskin, I.Essigke, *Optika i Spektr.*, **28**, 1006 (1975).
12. E.D.Palik, Handbook of Optical Constants of Solids, Academic Press, London (1985).
13. L.A.Ageev, V.K.Miloslavsky, T.I.Maksimenko, *Optika i Spektr.*, **36**, 133 (1974).
14. V.K.Miloslavsky, A.I.Rybalka, *Ukr. Fiz. Zh.*, **20**, 1612 (1975).
15. V.V.Mussil, Ye.T.Lemeshevskaya, V.V.Pilipenko, *Functional Materials*, **10**, 693 (2003).
16. J.Arends, J.Verwey, *Phys. Stat. Solidi (b)*, **23**, 137 (1967).
17. L.V.Gurvich, G.V.Karachevtsev, V.N.Kondratyev et al., Chemical Band Breakdown Energies: Ionization Potentials and Electron Affinity, Nauka, Moscow (1974) [in Rusisan].
18. L.A.Ageev, V.K.Miloslavsky, *Optical Engineering*, **34**, 960 (1995).

Фотоіндуковані явища у тонкоплівкових системах $Cu–PbI_2$ та $Cu–PbI_2$-халькогенідний склоподібний напівпровідник

В.В.Муссіл, К.Т.Лемешевська, В.В.Пилипенко

Наведено результати дослідження фотоіндукованих процесів у двох- і трьохшарових системах $Cu–PbI_2$ та $Cu–PbI_2$-халькогенідний склоподібний напівпровідник (Ge–As–S). Виявлено оборотні зміни оптичного пропускання систем $Cu–PbI_2$–Ge–As–S при їх послідовному опроміненні світлом з різними довжинами хвиль (442 і 633 нм). Знайдено, що опромінення систем лінійно поляризованим світлом, що слабо поглинається, призводить до утворення в них дифракційних періодичних структур. Явища, що спостерігаються, проаналізовано з урахуванням процесів фотодифузії Cu, утворення і руйнування дрібних металевих частинок у шарі PbI_2 та хвилеводного розповсюдження світла у плівковій системі.