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Long-wave light sensitivity of a thin film system based on PbI_2 and Cu

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Abstract. Photostimulated interaction in a sandwich-like thin film system based on PbI_2 and Cu (photodoping effect) makes it possible to use the system as a recording medium. On the other hand, since the layer consisting of copper nanoparticles embedded into the PbI_2 matrix is formed as a result of photodissolution of Cu film, this effect can be considered as an original way to produce nanocomposites. In this work, long-wave sensitivity of the PbI_2–Cu_2O–Cu system has been studied in conjunction with the structure of the PbI_2 film. It has been established that, in the $h\nu < E_g(PbI_2)$ spectral region the light absorption in PbI_2 film and the metal film photodissolution rate are higher for the less compact (more porous) PbI_2 films.

Keywords: photodoping, nanoparticles, nanocomposite, inorganic photoresist, thin film, copper, lead iodide, Wemple and DiDomenico single-oscillator model.

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1. Introduction

Investigation of the effect of photostimulated interaction in semiconductor-metal systems (photodoping effect) is of a considerable scientific and practical interest [1, 2]. It is important part of fundamental physics of low-energy radiation influence on thin-film systems and impurities in solids. The effect was the basis in creation of specific recording media used as a high-resolution inorganic resist in electronics, optics, and as a medium for holography, data recording, *etc*. The best results in many applications have been achieved for the chalcogenide glassy semiconductor (ChGS) – Ag systems [1, 2].

The competitive silver-free PbI_2–Cu_2O–Cu recording medium was suggested in [3-5]. Its characteristics (sensitivity, resolution, stability) approach to those of the ChGS–Ag based media. It was achieved primarily due to controlled formation of the PbI_2–Cu interface. Comprehensive study of the interaction between PbI_2 and Cu films stimulated by light from the lead iodide fundamental absorption band allowed us to create the model of photodoping effect for this case [3, 4]. Based on this, the high-quality photolithography technology for the practically important metals and metalloceramics (Cr, Mo, W, Al, Cr-SiO, *etc*.) using PbI_2–Cu_2O–Cu photoresist system was also suggested [6].

An important feature of the PbI_2–metal based systems is that, unlike the ChGS – metal based systems, their light-generated photodoped layer is heterogeneous and consists of metal nanoparticles embedded in the polycrystalline PbI_2 matrix. The study of objects containing metal nanoparticles has considerable independent significance. Therefore, in view of its importance, the study of photostimulated interaction in the PbI_2–Me light-sensitive systems should be viewed in a broader context than just the study of these systems as a recording medium. In the papers [7, 8], we have shown that varying such parameters of deposition process as residual pressure in vacuum chamber P_{dep} and deposition

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rate V_{dep} has an essential effect on the structure of vacuum-deposited lead iodide films. By changing the structure of halide film, we were able to a certain extent control concentration, size and shape of copper nanoparticles in photodoped nc-Cu–PbI_2 layers obtained by exposition of PbI_2–Cu_2O–Cu system with the $h\nu > E_g(PbI_2)$ light [7, 8].

At the same time, interaction under the influence of long-wave light ($h\nu < E_g(PbI_2)$) is less studied and understood. Meanwhile, some interesting practical results using such light have been obtained. In [9], the full color and/or dichroic recording process was implemented under exposing the PbI_2–Me systems with the island metal film by the $h\nu < E_g(PbI_2)$ light. Authors [10, 11] created *nc*-Ag–PbI_2 and nc-Cu–PbI_2 nanocomposites from layered Ag–PbI_2 and Cu–PbI_2 systems using the $h\nu > E_g(PbI_2)$ unpolarized light. Then they exposed it to the linearly polarized $h\nu < E_g(PbI_2)$ light. As a result, the periodic diffraction structures consisting of the metal nanoparticle rows oriented in parallel to the electric vector of exposing light were formed. This paper presents the results of studying the spectral dependences of the light-sensitivity for PbI_2–Cu_2O–Cu systems under action of light with quanta energy $h\nu < E_g(PbI_2)$. Special attention was given to studying the influence of semiconductor film preparation conditions on the long-wave sensitivity of these systems.

2. Experimental procedure and results

The sandwich-like samples of PbI_2–Cu_2O–Cu systems and companion PbI_2 films on K-8 glass substrates were prepared as described in [3, 4]. At first, the copper film was deposited at the pressure in the vacuum chamber $P_{dep} = 3\cdot10^{-3}$ Pa with the deposition rate $V_{dep} = 1.0$ nm/s. Then, the Cu_2O film was formed on this film by oxidation of Cu film in air. This step is necessary to obtain highly sensitive reproducible systems [3, 4]. Finally, the PbI_2 film was deposited. In various vacuum cycles the V_{dep} amounted between 0.1 and 1 nm/s, and P_{dep} between $3.0\cdot10^{-3}$ Pa and $1.5\cdot10^{-2}$ Pa. This process produced the PbI_2–Cu_2O–Cu samples in which the Cu and Cu_2O films had identical characteristics, while characteristics of the PbI_2 film varied from sample to sample. The thicknesses of the PbI_2, Cu_2O, and Cu films were 50, 4, and 40 nm, respectively.

The systems were exposed by light from the spectral region $h\nu$=1.77…2.3 eV ($E_g(PbI_2)\approx$ 2.3…2.4 eV for thin films of lead iodide at room temperature [12-15]). The metal film expenditure kinetics during irradiation was monitored using photometry: changes in the transmission coefficient T were measured at λ = 1500 nm, and light sensitivity S was in proportion to the rate of its change.

The optical techniques (ellipsometry and photometry *R-T* technique) were used to obtain structural information of the PbI_2 films. The thickness and optical constants of the as-deposited PbI_2 films were determined using ellipsometric measurements at the wavelength 633 nm. The KSVU-23 spectral complex and calculation method described in [16] were used to determine the spectral dependences of the refractive index n and absorption index k for the PbI_2 films in the 400…1000 nm range.

As it was demonstrated using measurements of the PbI_2 films density and investigations of $n(h\nu)$, $k(h\nu)$ dependences in the $h\nu > E_g(PbI_2)$ spectral region [7, 8], the greater the deposition rate and especially the residual pressure during the deposition of PbI_2 films, the less dense and more disordered films are formed. Fig. 1 shows the spectral dependences of light-sensitivity S for two systems with the identical Cu and Cu_2O films but with differently deposited PbI_2 films. (The figure shows the data for the systems in which the properties of PbI_2 films differ the most among the investigated set of samples.) The PbI_2 film deposited at $V_{dep} = 1.0$ nm/s, $P_{dep} = 3.0\cdot10^{-3}$ Pa has n (λ = 633 nm) = 2.84, and the PbI_2 film deposited at $V_{dep} = 1.0$ nm/s, $P_{dep} = 1.5\cdot10^{-2}$ Pa has n (λ = 633 nm) = 2.52. The estimated values of porosity consists 0.05 and 0.23, respectively. As can be seen, the sensitivity for the system with less dense PbI_2 film is sufficiently (several times) higher. For both systems, the edge of the sensitivity spectrum is satisfactory described with $S \sim (h\nu - h\nu_0)^2$ quadratic dependence, which is analogous to the Fowler dependence for internal photoemission of charge carriers from metal into semiconductor. The $S(h\nu)$ dependence of the same kind was obtained in PbI_2–Cu system without an intermediate oxide layer [1]. The $h\nu_0 = 1.69$ eV value obtained here for the system with intermediate oxide layer and dense PbI_2 film is quiter close to the $h\nu_0 = 1.65$ eV value [1] obtained for the PbI_2–Cu system without an intermediate oxide layer. Substitution of the dense PbI_2 film with the porous one lowers the $h\nu_0$ value at ~0.4 eV. In [1], it was assumed that the $S \sim (h\nu - h\nu_0)^2$ spectral dependence in the long-wave range of the spectrum is determined by photoemission from metal, which leads to changes in the electric field at the contact and to the transfer of the metal ions. In this case, the $h\nu_0$ value can be regarded as the height of the barrier for internal photoemission for metal–semiconductor contact. We also may assume that in the case of the PbI_2–Cu_2O–Cu systems the spectral course of the sensitivity is determined by the internal photoemission of charge carriers from metallic film.

To clarify the question of the difference among the long-wave sensitivity characteristics of the PbI_2–Cu_2O–Cu systems with different PbI_2 films, we additionally investigated the dispersion of refractive index n within this spectral region for the PbI_2 films deposited at various sets of the deposition process parameters. This is particularly useful in the spectral region where the values of the absorption index are small and difficult to measure, especially at low film thickness. Besides this technical difficulty in determining the small values of absorption index, there is also the methodological difficulty. Methodological circumstances are as follows:

in the presence of scattering (which is always inherent in varying degrees in all the samples) the photometric measurements based on the transmitted light intensity determination actually obtain the value of extinction index that contains the components of the absorption and scattering. Thus, the smaller the true value of the absorption index, the greater the relative contribution of the scattering in the measured value of the extinction index.

The refractive index dispersion data below the interband absorption band of many covalent and ionic compounds is rather well described by the Wemple and DiDomenico single-effective-oscillator model with two parameters E_0 and E_d [17]:

$$n^2(h\nu) = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2}. \qquad (1)$$

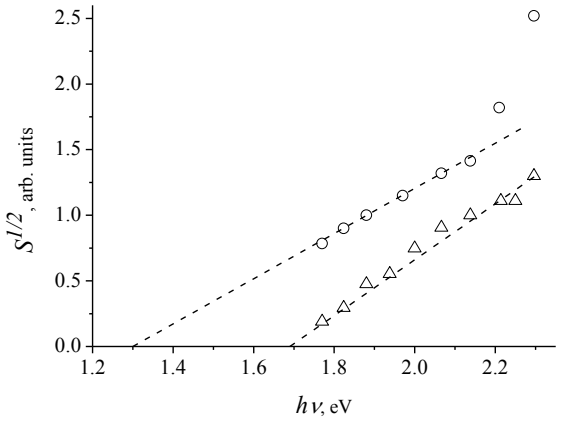

Fig. 1. Spectral dependences of light sensitivity (S) in spectral region $h\nu < E_g(PbI_2)$ for PbI_2–Cu_2O–Cu system in which PbI_2 film is deposited at $P_{dep} = 3.0 \cdot 10^{-3}$ Pa, $V_{dep} = 1$ nm/s (triangles) and $P_{dep} = 1.5 \cdot 10^{-2}$ Pa, $V_{dep} = 1$ nm/s (circles).

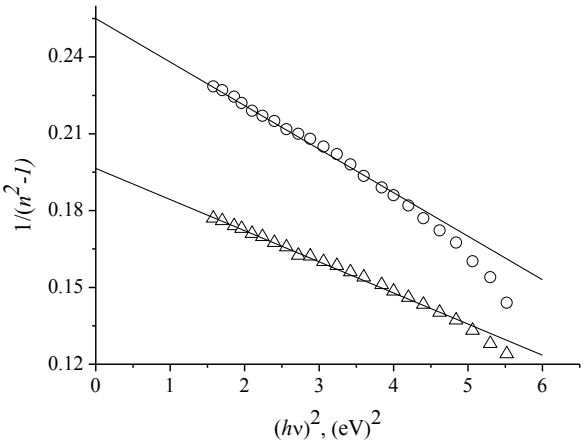

Fig. 2. Description of the refractive index dispersion on the basis of the Wemple and DiDomenico single-oscillator model. PbI_2 film is deposited at $P_{dep} = 3.0 \cdot 10^{-3}$ Pa, $V_{dep} = 1$ nm/s (triangles) and $P_{dep} = 1.5 \cdot 10^{-2}$ Pa, $V_{dep} = 1$ nm/s (circles).

The parameter E_d is the oscillator strength or dispersion energy which is a measure of the strength of interband optical transitions. The oscillator energy E_0 is the average energy gap. To establish how well the dispersion of our PbI_2 films is simulated by the Wemple and DiDomenico single-oscillator model, we plotted dispersive $n(h\nu)$ dependence as $1/(n^2 - 1)$ versus $h\nu$. The experimental values for the PbI_2 films with estimated porosity p of 0.05 and 0.23 are given in Fig. 2 by circles and triangles. The value of E_0 and E_d can be directly determined from the slope $(E_0E_d)^{-1}$ and the intercept on the vertical axis (E_d/E_0). These values are $E_d = 20.14$ eV, $E_0 = 4.04$ eV for the most dense film, $E_d = 15.1$ eV, $E_0 = 3.86$ eV for the least dense film. As seen, for the film with $p \approx 0.05$ good description by the dependence (1) occurs at $h\nu \leq 2.2$ eV, and for the film with $p \approx 0.23$ at $h\nu \leq 2.0$ eV. Thus, the more porous and disordered PbI_2 film is, the longer are the wavelengths at which deviation of the films' refractive index dispersion from the Wemple and DiDomenico single-oscillator model starts. This indicates that in less compact PbI_2 film the increase of absorption starts at lower photon energies. That is, in these films the tail of absorption spectrum is more extended (and definitely greater in magnitude). The growth of this long-wave absorption is due to the increased density of states in the band gap due to the increase in the number of structural defects and impurities in the less compact halide films. As seen, the increase in the number of the gap states also reduces the value of the average energy gap parameter E_0.

3. Conclusions

The less dense PbI_2 films deposited at higher pressure and at greater deposition rate show more pronounced deviation of the refractive index dispersion in the $h\nu < E_g(PbI_2)$ region from the Wemple and DiDomenico single-oscillator model. The most probable cause for this phenomenon is stronger absorption in this spectral region due to the greater structural and compositional disordering in those films.

There is correlation between the PbI_2 film $n(h\nu)$ dispersion curves in the $h\nu < E_g(PbI_2)$ region and the long-wave sensitivity of the PbI_2–Cu_2O–Cu systems – the more pronounced is deviation, the higher is the sensitivity.

These results show that the energy states in the band gap of halide semiconductor play significant role in the long-wave light sensitivity of the thin film systems based on lead iodide and copper.

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