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Effect of Heat Treatment on the Photosensitivity of Polycrystalline PbTe Films AND PbS

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Abstract. PbTe and PbS films obtained on different substrates. It has been established that long-term heat treatment of PbS films leads to a change in the sign of the photovoltage at $h\nu = 0.55$ eV, and in the long-wavelength region of the spectrum at $h\nu = 0.3$ eV, the photoconductivity has a small maximum, which is due either to impact ionization or the generation of charge carriers from deep bands.

Keywords. films, PbTe, PbS, polycrystal, heat treatment, charge carrier concentrations, electrical conductivity

Introduction. Despite a large number of experimental and theoretical works, the physical processes responsible for photoelectric phenomena occurring in polycrystalline A_4B_6 films still remain unexplored, since this is due to the apparent inconsistency of the experimental data obtained by various authors [1-4]. The structures and properties of intercrystalline barriers in A_4B_6 materials are even more uncertain. It is reported in [5-7] that oxygen is concentrated on the surface of lead sulfide films and in intercrystalline interlayers, but does not penetrate into the volume of crystallites. Oxygen in such films can form chemical compounds such as $PbSO_4$ and PbO , $PbSO_4$, PbO on their surface and in intercrystalline interlayers. Heat-treated films of lead chalcogenides are very similar in their properties, which is probably why they have a non-uniform distribution of impurities both over the layer thickness and in the intergranular barrier.

Methodology. In this regard, let us consider the possibilities of using the technique [8] for measuring the spectral dependence of photoconductivity and photo-EMF as applied to PbS and PbTe films. Films obtained by deposition in a vacuum followed by their activation in an oxygen-containing atmosphere were studied [9].

Experimental results and their discussion. Figure 1 shows the dependence of photoconductivity (curve 1) and photo-EMF (curve 2) on the energy of the incident light quantum for PbTe films obtained on glass-ceramic substrate. In these films, the photo-EMF is more sensitive to the state of the surface (curve 2) than the

photoconductivity (curve 1). This indicates a large asymmetry of the barriers near the surface, which is formed during processing. The asymmetry of barriers has a different relationship with the state of the surface in PbTe films deposited on an oxidized silicon surface. In such films, an inversion of the photo-EMF sign is observed in the region at $h\nu = 0.4$ eV (Fig. 2, curve 2).

Next, the effects of the substrate and heat treatment conditions on the photoelectric properties of PbS films were studied. On fig. 3 and 4, respectively, show the photo-EMF and PC spectra for these films deposited on polycor. The films were thermally treated for 10 and 20 min in an oxygen-containing atmosphere. As can be seen from the figure, long-term heat treatment of PbS films leads to a change in the photo-EMF sign to the opposite at $h\nu = 0.55$ eV (Fig. 3, curve-3). The shape of the curves of the PT spectra does not change significantly with increasing heat treatment time (Fig. 4, curves 1, 2). In the long-wavelength region of the spectrum at $h\nu = 0.3$ eV, the phase transition has a small maximum, and some decrease is observed with increasing photon energy. Starting from $h\nu = 0.75$ eV, as the energy of a light quantum increases, the FP increases. Such an increase in photoconductivity can be due either to impact ionization or generation of charge carriers from deep bands [] or from heterojunctions between crystallites and other compounds that form on the film surface and in intercrystalline interlayers during heat treatment. Then the film surface was removed by plasma etching, and the PC and photo-EMF spectra were again measured. Etching leads to the disappearance of the



sign inversion and an increase in the photo-emf (Fig. 3, curve 2). This can be explained by the fact that before etching on the film surface, the barriers had opposite polarities. During plasma etching, a thin layer of the film surface is removed, and thereby the contribution of barriers that give photo-EMF of opposite polarity is reduced. The remaining barriers generate photo-emf predominantly of one polarity, which contributes to its increase. This situation is apparently close to that in the case of CdTe after treatment with chlorine [].

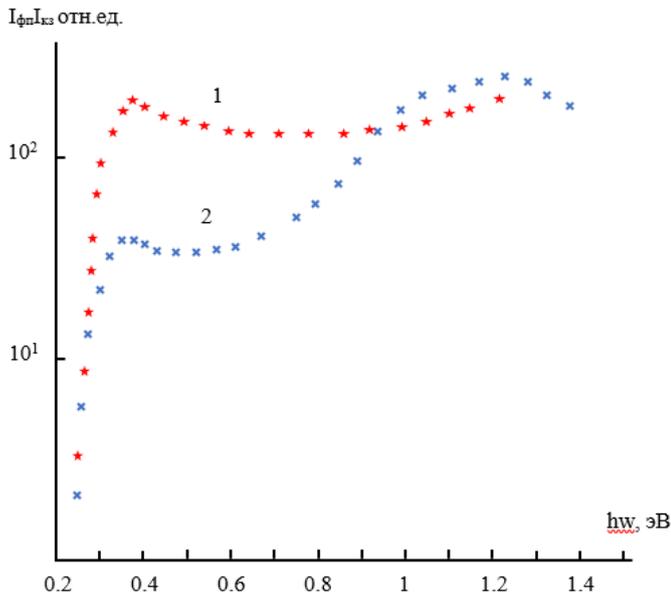


Fig. 1. Spectra of phase transition (1) and I_{cs} (2) for PbTe films obtained on glass-ceramic substrate. $T=300K$

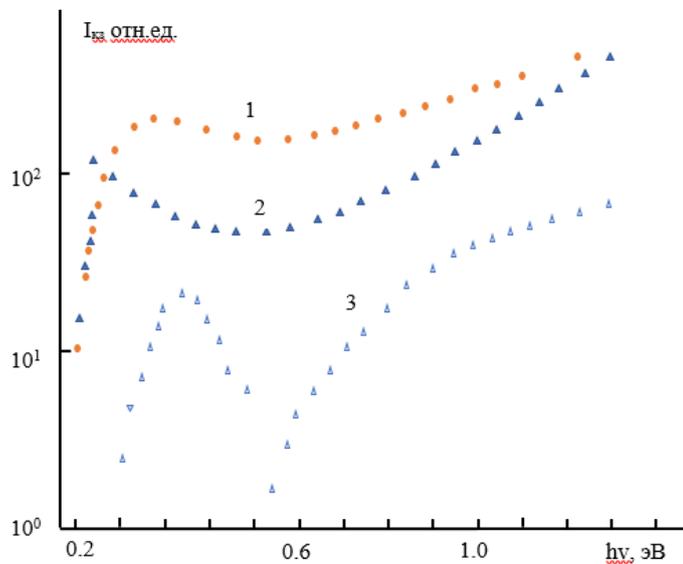


Fig.2. FP spectra (1) and I_c (2) for PbTe films obtained on a SiO_2-Si substrate. $T=300K$

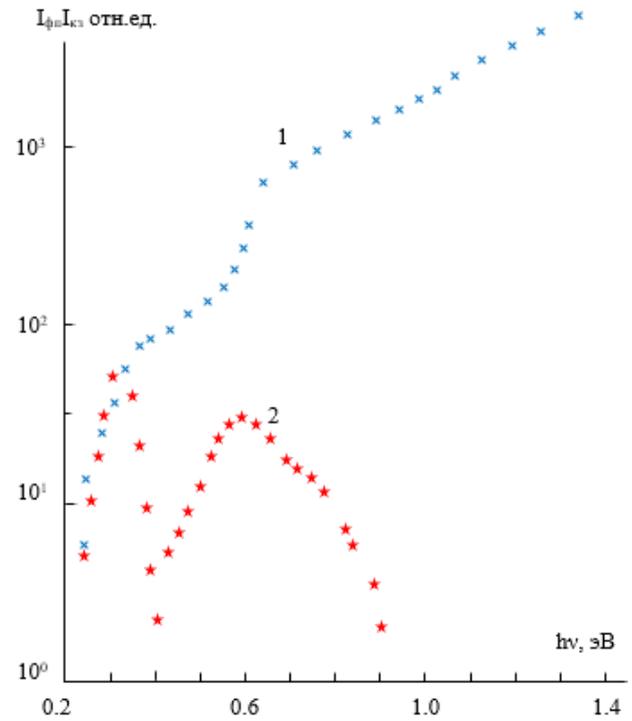


Fig. 3. Photo-EMF spectra for PbS films obtained on polycore. 1 - after heat treatment for 10 min in an oxygen-containing atmosphere, 2 - after heat treatment for 20 min and plasma etching, 3 - after heat treatment for 20 min.

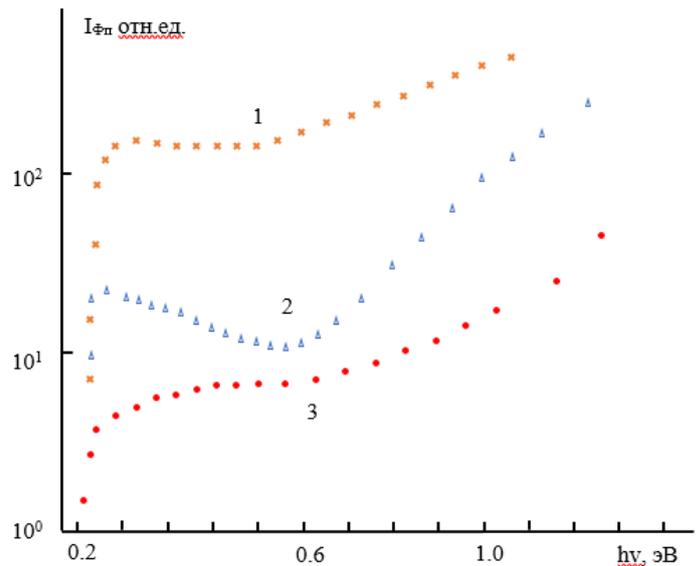


Fig. 4. FP spectra for PbS films obtained on polycor; 1 - after heat treatment for 10 min in an oxygen-containing atmosphere; 2 - after heat treatment for 20 min; 3 - after heat treatment for 20 min and plasma etching.



In films deposited on $\text{SiO}_2 - \text{Si}$, more asymmetric barriers are obtained, which change the polarity of the photo-EMF under back illumination at $h\nu = 0,8 \text{ eV}$ (Fig. 5, curve 3).

An analysis of the PC and photo-EMF spectra showed that with increasing heat treatment time, the asymmetries of effective barriers on the surface of PbS films obtained on polycore change, and in films deposited on $\text{SiO}_2 - \text{Si}$, barriers of a different asymmetry are formed near the substrate, although the possibility of generation is not ruled out. carriers from deep levels arising in the PbS - SiO_2 heterojunction.

Due to the small size of crystallites compared to the length of the diffusion displacement of holes in them, the recombination conditions on the film surface can significantly affect the photoconductivity and photo-EMF of the film. In our films, the recombination conditions change: on glass-ceramic they are almost the same in the region of 1.1 - 1.4 eV, on $\text{SiO}_2 - \text{Si}$, the built-in field separates the carriers, therefore, the closer to the surface, the more effective the separation of carriers. This indicates a disordered structure in which the barrier passes from one direction of anisotropy in SiO_2 to the opposite one on the free surface

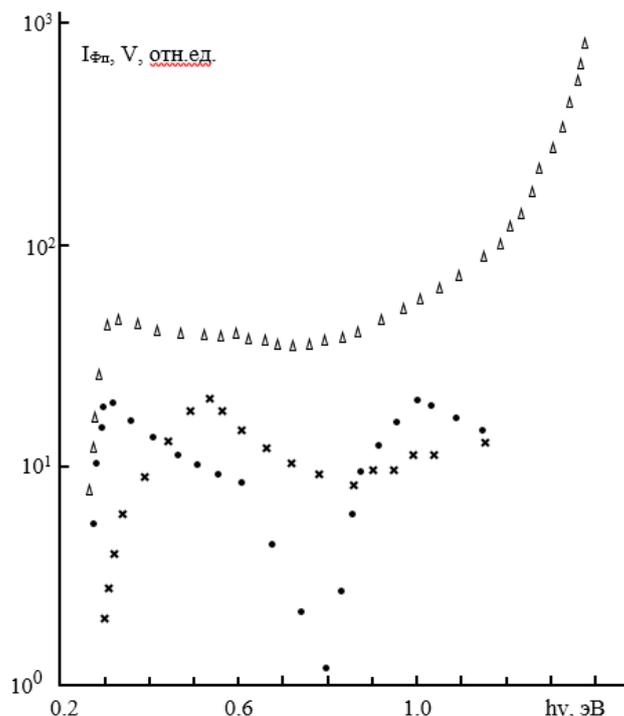


Fig.5. FP spectra (1) and photo-EMF (2,3) for PbS films obtained on $\text{SiO}_2 - \text{Si}$: 1 - after heat treatment for 10 min; 2 - with rear and 3 - with front lighting.

Thus, the complex technique used by us has shown sensitivity to the technology of fabrication and processing of layers, which makes it possible to use it to study the properties of films of A_4B_6 semiconductor compounds.

Conclusions. The technique for measuring the spectral dependence of the photon capture cross section, photoconductivity, and photo-EMF was also applied to the study of the photovoltaic properties of PbS films and $PbTe$ on glass-ceramic, polycor, and SiO_2 substrates obtained by vacuum deposition with their subsequent activation in an oxygen-containing atmosphere, and it was found that there are asymmetries of effective barriers on the PbS surface with increasing heat treatment time.

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