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Application of hot isostatic pressing to improve the optical performance of polycrystalline zinc sulfide

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The hot isostatic pressing of zinc sulfide, obtained by chemical vapor deposition technology, are studied to improve its quality characteristics. As a result of the studies carried out in the visible and near IR regions of the spectrum, the transmission of the treated samples was increased by 6–7 times compared to the untreated ones. In the wavelength range of $3-10\,\mu$m, the light transmission of the treated samples reached the theoretical limit.

Keywords: chalcogenides, zinc sulfide, chemical vapor deposition, hot isostatic pressing.

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The enhancement of capabilities of optoelectronic systems and complexes (specifically, the capacity for simultaneous operation in visible and IR ranges) in one of the priorities of optical and optoelectronic instrument engineering. Wide-gap $A^{II}B^{VI}$ semiconductors are traditionally used to fabricate IR optics elements. Chalcogenides ZnS and ZnSe hold a special position in this group: they feature a combination of unique properties, and their CVD (chemical vapor deposition) synthesis procedure has already been perfected. Since ZnS withstands significantly higher mechanical and thermal loads without degradation of optical characteristics, it is a better fit than ZnSe in certain applications.

It is known [1,2] that the CVD technique provides better results than high-temperature powder pressing and sublimation–condensation growth. However, ZnS synthesized this way is insufficiently transparent in the visible range due to radiation scattering by optical inhomogeneities forming in the process of synthesis [3]. Even when its density exceeds 99% of the theoretical maximum, pores with a characteristic size of $\sim 100-150$ nm remain in the bulk of the material. Polycrystalline CVD-ZnS transparent in the IR range and opaque in the visible region is known as FLIR grade CVD-ZnS, where FLIR stands for „forward looking infrared“.

The characteristics of polycrystalline zinc sulfide may be enhanced by subjecting it to further HIP (hot isostatic pressing) processing. Structural defects in the bulk of the material, the most significant of which are internal pores, are eliminated as a result of such processing, and the maximum transmission in the $0.4-13.5\,\mu$m spectral range is achieved. HIP also has a positive effect on the strength properties of CVD-ZnS. The produced material is known as MS grade CVD-ZnS, where MS stands for „multispectral“.

Polycrystalline zinc sulfide of the indicated grades is widely available at present in the overseas commercial market. However, the only thing known from published sources is that high-quality MS grade material is produced using HIP (see, e.g., [4,5]). Exact process parameters are not reported.

In view of this, the aim of the present study was to determine practical parameters of the HIP process for conversion of FLIR grade ZnS into MS grade ZnS. CVD-ZnS samples were provided by LLC „Promlab“.

Samples were cut from one slab and were $40 \times 40 \times 4$ mm in size. Two types of samples were examined: uncoated ones and samples wrapped in platinum foil with a thickness of approximately $30\,\mu$m. It was assumed that this metallic coating should inhibit grain growth in HIP processing [6].

An HIP press with the following parameters was used: the working space of the high-pressure chamber was 250 mm in diameter and 350 mm in height, the maximum operating pressure was 2500 bar, the maximum operating temperature was 2000°C, and the working medium was 99.998% pure argon.

The HIP procedure was a standard one: samples were introduced into the chamber; the working volume was filled with gas at normal temperature; the temperature and pressure were raised in a controlled manner; samples were held at fixed temperature and pressure values for a certain time and then cooled at a predefined rate. The characteristic diagram of temporal variation of pressure and temperature recorded by the control system of the press within a complete HIP processing cycle is presented in Fig. 1.

The effects of HIP processing were examined in cycles with a holding time of $8-12$ h at a temperature of $985-1020^\circ$C and a pressure of $1500-1600$ bar. Prior

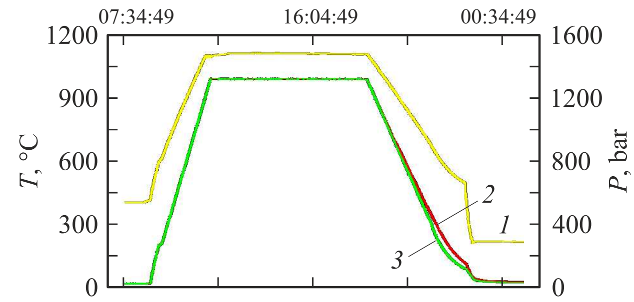

Figure 1. Plots of pressure (*1*) and temperature in the upper (*2*) and lower (*3*) furnace zones in a typical hot isostatic pressing cycle.

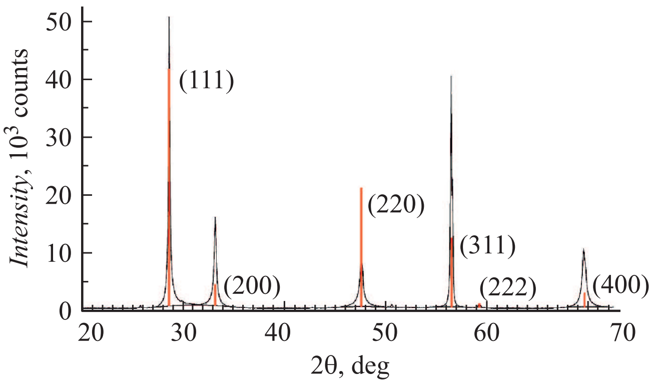

Figure 2. Diffraction pattern of the CVD-ZnS sample. Card PDF 03-065-0309 from the PDF-4 database was used for peak indexing.

to introduction into the high-pressure vessel of the press, samples were fitted separately into specialized assemblies.

The holding pressure was set significantly below the maximum. The results obtained in [7] were take into account: it was found in this study that, under otherwise equal conditions, the application of the maximum pressure provides a $\sim 10\%$ advantage in light transmittance compared to the value that may be achieved under a pressure of 2000 bar. This advantage may be compensated by increasing the holding time, and a reduction in pressure makes HIP processing much more economically efficient.

Samples with a polished surface were used at all stages of HIP processing. Polishing, which is needed for subsequent examination of the optical properties, was performed after pressing in accordance with the standard optical procedure.

According to [7], CVD-ZnS has a cubic lattice modification known as sphalerite. The results of examination with a BRUKER D8 ADAVANCE diffractometer revealed that the diffraction patterns of samples (see a typical one in Fig. 2) feature only the peaks belonging to this crystalline phase. No signs of the hexagonal modification (wurtzite) were detected.

The samples were then examined using an Altami Polar 3 optical microscope fitted with a digital camera with its operation controlled in Altami Studio 3.5. The same dark field was obtained for all samples in imaging in polarized light with crossed polarizers. This is indicative of optical isotropy of the produced material, which is typical of its cubic modification.

A practical pressing regime was determined in the search for the optimum HIP processing conditions for the present case: temperature and pressure should fall within the intervals of 985–1000°C and 1500–1600 bar. The samples become transparent in the visible range as a result of this treatment; thus, FLIR grade zinc sulfide was converted into MS grade ZnS.

An SF-2000 spectrophotometer was used to measure the transmission spectrum in visible and near IR ranges (in the 300–1100 nm interval). Figure 3, *a* shows the theoretically possible maximum transmission (*1*) and the transmission spectra for samples without coating (*2*), with platinum coating (*3*), and before HIP processing (*4*). Note that the curves for other samples are similar in nature and differ by no more than 5% in transmission. No systematic influence of the process parameters on the attainable transmission coefficient was found.

An FSM 1201 Fourier spectrometer was used to determine the transmission spectrum in the middle IR range (3–13 μm). Figure 3, *b* presents the obtained transmission spectra for the same samples in the same format.

Figures 3, *a* and *b* demonstrate that the proposed HIP processing regimes provide an opportunity to improve considerably the light transmission characteristics within the entire transparency region. Specifically, while the transmis-

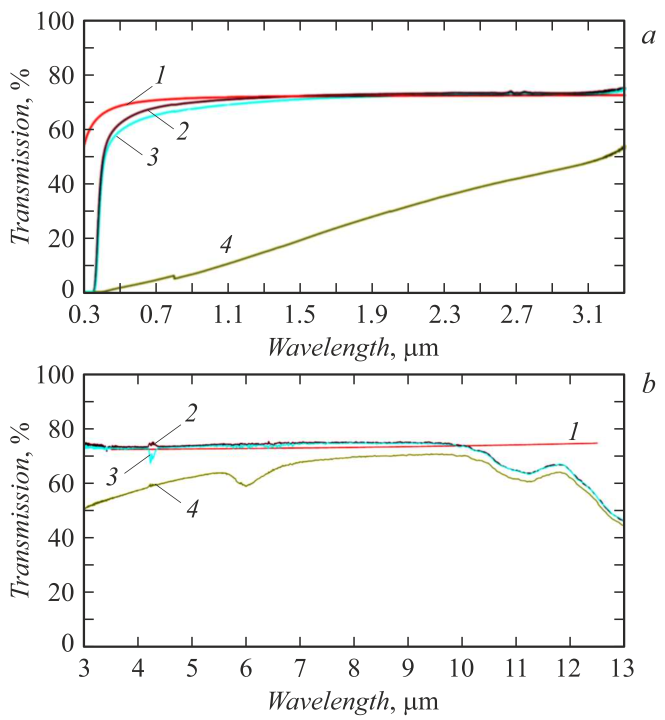

Figure 3. Transmission spectra of ZnS samples in visible, near IR (*a*), and middle IR (*b*) ranges. *1* — Theoretical maximum, *2* — uncoated sample, *3* — coated sample, *4* — sample before HIP processing.

sion of the initial FLIR grade ZnS sample in the visible range does not exceed 5% (Fig. 3, *a*), the transmission for MS grade ZnS after pressing increases to 60% at a wavelength of 0.4 μm and 68% at 0.8 μm, approaching the theoretical limits of 67 and 70%, respectively. In the near IR range, the transmission of the initial FLIR grade ZnS sample is no higher than 10%; following HIP, it increases to 70%, which is almost equal to the theoretical limit (71%). It should be noted that platinum coating did not provide any additional enhancement of transmission values achieved by uncoated samples. HIP processing of FLIR grade ZnS did also raise the transmission all the way up to the theoretical maximum in the especially important middle IR range (Fig. 3, *b*) at wavelengths of 3–10 μm.

Thus, technological regimes of hot isostatic pressing of zinc sulfide for enhancement of its qualitative characteristics (most importantly, light transmission in the visible and near IR ranges) were examined. A practical pressing regime was determined in the search for the optimum HIP processing conditions for the present case: temperature and pressure should fall within the intervals of 985–1000°C and 1500–1600 bar. HIP processing in this regime provides an opportunity to achieve a 6–7-fold enhancement of light transmission in the visible and near IR ranges. The transmission of processed samples in the middle IR range at wavelengths of 3–10 μm reached its theoretical maximum.

Conflict of interest

The authors declare that they have no conflict of interest.

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